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R. P. FROHMBERG
W. J. BARNETT
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FOREWORD

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ABSTRACT

The phenomenon of delayed failure in steel has been correlated with the presence of electrolytically introduced hydrogen. Delayed failure may occur over a wide range of relatively low applied stresses and this stress range is dependent upon strength level, notch acuity and aging time after the introduction of hydrogen. The observed reductions in ductility are a function of both the depth of hydrogen penetration and the degree or severity of hydrogen embrittlement. The effects of aging with and without load have demonstrated the necessity of exceeding some minimum critical stress in the presence of hydrogen to embrittle steel. A bainitic structure was shown to behave in a fashion similar to that of tempered martensite, except that the overall embrittlement appeared less severe.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Robert W. Rowden, Major, USAF

for LESLIE B. WILLIAMS
Colonel, USAF
Chief, Aeronautical Research Laboratory
Directorate of Research

PREFACE

The use of the high strength levels which steel is capable of developing has been seriously limited by the several types of embrittlement which have been encountered. Only recently have designers passed the 200,000 psi strength level; and in order to realize the full potential of high strength steels, a comprehension of the accompanying losses in ductility must be attained. A better understanding of the "500°F embrittlement" has been gained by recent work, and this is a material contribution toward the more efficient utilization of steels heat treated to high strength levels. However, another type of embrittlement now stands as a major obstacle to the continued development of higher strength levels in alloy steels. The occurrence of hydrogen embrittlement has been known for some time, but only recently has the phenomenon of delayed service failure received note. This is a particularly insidious type of failure in that spontaneous brittle fracture takes place in parts which have been heat treated to high strength levels. A better appreciation of the problem of delayed failure would do much to permit the more widespread use of steel at the high strength levels under consideration.

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I INTRODUCTION

A. THE PROBLEM

Many problems associated with embrittlement are met in the use of alloy steels heat treated to high strength levels. In recent years, particularly in the aircraft field, engineers have been working toward higher strength levels which makes an understanding of the various forms of embrittlement of increasingly greater importance (1). One of the phenomena encountered when steels are heat treated to high strength levels is the occurrence of brittle delayed failures in service. For example, electroplated steel bolts heat treated to high strength levels have shown delayed failures at the root of the threads or in the head fillet; similarly, other electroplated parts have been known to fail in a brittle fashion under the influence of static loads. This has been observed under relatively mild service conditions despite precautions taken to minimize or eliminate the commonly known embrittling factors such as poor fillet design and improper thermal treatments. Service failures have been reported in plain carbon steel springs heat treated to high strength levels and subsequently plated or pickled.

In view of these observations, it seems apparent that the phenomenon of delayed failure under static load is usually associated with:

1. Steels heat treated to high strength levels.

2. Exposure to a hydrogen environment in processing history.

This study was undertaken in an attempt to correlate these known brittle delayed service failures under static loads with the presence of hydrogen in a 4340 steel heat treated to several high strength levels.

B. REVIEW OF PREVIOUS EXPERIMENTAL WORK

The published literature actually contains relatively little on the subject of delayed failure per se, but many studies have been made of the effects of hydrogen on the ductility of steel. It is felt that if an explanation of delayed failure based on the presence of hydrogen is offered, it must be consistent with the other embrittling effects of hydrogen. The following is a cursory review of

some of the many observations of the effects of hydrogen. An exhaustive literature survey has been made by Buzzard and Cleaves (2) and other work includes summaries of previous information together with relatively abridged bibliographies (3, 4, 5 and 6).

Hydrogen may be introduced into steel from a variety of sources which might be divided into natural and artificial origins. Considering first the congenital sources, the steel-making process itself is one major origin of hydrogen (7, 8) and it is particularly troublesome in large section sizes (9, 10). Here the presence of hydrogen is manifest as flakes or substantial reductions in ductility (11). Other processing operations such as pickling (12, 13) and electroplating (14, 15, 16) are recognized sources which have been studied. Welded sections sometimes show loss of ductility and flakes, both of which have been attributed to the presence of hydrogen.

There are several laboratory techniques for the deliberate introduction of controlled amounts of hydrogen into steel. Specimens may be heated in the vicinity of 2000°F in hydrogen at or near 1 atmosphere pressure. Some investigators heat to lower temperatures in hydrogen under pressure. Electrolytic charging is also commonly used, sometimes with a "poison" to enhance the pick-up of hydrogen by the specimen. Along these same lines, pickling in solutions of various concentrations has been shown to be effective in charging specimens with hydrogen. One investigator has shown (17) that electrolytic charging and the introduction of hydrogen under pressure at 600°C both gave the same embrittling effect, as measured by reduction in area in tensile testing.

The equilibrium solubility of hydrogen in ferritic steel at room temperature has not been determined, but from an extrapolation of data at higher temperatures it is thought to be extremely small. On the other hand, large amounts of hydrogen may be introduced and retained in steel. In one instance, for example, a concentration of 65cc/100 gm[a] (18) was attained by electrolytic charging, while in another case a 5" x 5" steel billet retained up to 5cc/100 gm eight months after fabrication (9). Thus, relatively large quantities of hydrogen, well in excess of equilibrium solubilities, may be retained in steel.

One of the most curious features of this problem is the fact that austenitic steels are relatively immune to the embrittling effects of hydrogen (19). In one instance, (20) concentrations of 25cc/100 gms were needed to produce measurable

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a. The concentration of hydrogen in steel may be given in several ways. The designation used here will be cc of hydrogen at standard pressure and temperature per 100 grams of steel (cc/100 gm). One cc/100 gm = 0.0787 relative volumes = 0.00009 weight percent ≈ 0.9 parts per million.

changes in the ductility of an austenitic steel. By contrast, four to six cc/100 gms is sufficient to produce very severe embrittlement in ferritic steels (17, 21, 22).

Another interesting aspect of hydrogen in steel is the effect of cold working. Darken and Smith (23) showed that the maximum amount of hydrogen absorbed (in pickling) increased linearly by increasing the degree of cold working prior to pickling. They also found that the rate of absorption showed a similar dependence on the degree of deformation. The evolution of hydrogen is accelerated during cold working (24, 25). Bend tests have shown that when cold worked, steel is more susceptible to embrittlement than when annealed (16, 26).

Several experiments have been reported in which a permanent change in steel seems to have occurred as a result of charging with hydrogen. A 1/8'' thick steel cylinder (27) in a steel backup shell was first tested with oil at 295,000 psi pressure with no permeation observed. After pressurizing with hydrogen at 59,000 psi, the cylinder permitted the passage of hydrogen at 100 psi and oil at 59,000 psi. Bridgman (28) demonstrated that hydrogen could be made to pass through a steel wall when under a pressure of 128,000 psi. In neither case was there any apparent damage to the metal.

A more vivid demonstration along similar lines has been given (18). Steel wires were electrolytically charged, immersed in molten brass, sectioned and prepared metallographically to show that some of the molten brass had permeated to a considerable depth below the surface of the steel wire. When the charged hydrogen was removed by aging 10 hours at 750°C, penetration upon immersion in brass was not observed. When subjected to severe electrolytic charging (21, 24), surface bursts, presumably the result of hydrogen pressure build up, have been found.

It appears that the elastic behavior of steel during tensile testing is unaffected by the presence of hydrogen, but some changes do occur in the plastic region of the stress-strain curve. Several investigators (17, 21, 29) have clearly demonstrated that increasing amounts of hydrogen reduce the fracture strain; i.e., the stress-strain curve is cut off short of its normal course for unembrittled material. More detailed studies (30) have revealed a slight lowering of the upper and lower yield points and a decrease in the strain hardening exponent of a pickled low carbon steel. Statistical analysis of the data was used to verify the fact that the small changes observed were real.

The strong dependence of hydrogen embrittlement on strain rate and testing temperature has been verified by a number of investigations (20, 30, 31, 32). For example, it is well known that charged specimens which exhibit embrittlement at moderate strain rates and temperatures can be made to show normal ductilities when tested at high strain rates or at low temperatures. Neither impact testing nor the standard indentation hardness tests appear to be of any practical value as an index of hydrogen embrittlement. Presumably this is due to the fact that both

tests are conducted at relatively high strain rates.

The strength level to which steel is heat treated also has a strong effect on the susceptibility to hydrogen embrittlement. Hobson and Sykes (17) showed that for a given concentration of hydrogen, the reduction in area in the tensile test first decreased then increased rapidly as the strength level was increased. Similar relationships have been reported for the incidence of delayed failure of electroplated lockwashers (15, 33).

Numerous studies have been made in which recovery from the embrittled state has been observed on aging, usually at room temperature (19, 21, 22, 24, 34). Various criteria, such as bend tests, cup tests, elongation, and reduction in area have been used as an index of embrittlement. In general, the degree of embrittlement decreased with increasing aging time and complete recovery of ductility was eventually attained if the charging conditions were not too severe. On the other hand, when the strength level was high and the charging conditions were severe, baking treatments which were effective in producing recovery at lower strength levels were not able to produce complete recovery at the higher strength levels (35). Occasionally, a minimum has been observed in the aging curve at short aging times, i.e., an initial decrease in ductility prior to recovery. Aging at elevated temperatures accelerates the recovery process while for all practical intents and purposes the aging process may be stopped completely if the temperature is low enough.

The evolution of hydrogen during aging has also been studied (36). At a given temperature, initial evolution was rapid and decreased with time to a very low value. When the temperature was raised, rapid evolution again occurred which diminished with time. It appeared that a discrete portion of the total hydrogen content was evolved at each succeedingly higher temperature. The authors stated that the evolution was a function of temperature alone and was not rationally related to the quantity of gas present, nor did it represent an approach to equilibrium solubility. The loss of hydrogen was associated with the opening of lattice rifts as the temperature was raised.

Studies have been made on the delayed failure of electroplated lockwashers (15, 33). A strong dependence of propensity towards delayed failure on strength level was demonstrated. It was also shown that delayed failures could be minimized or eliminated by baking at 400°F after plating. In conical disc tests (37), a strong dependence of test life under static load on hardness was shown. A number of heats of steel were studied and no mention was made of the addition of hydrogen. Evidently, delayed failure may occur in the absence of artificially introduced hydrogen.

C. REVIEW OF PROPOSED MECHANISMS

One of the most popular explanations for hydrogen embrittlement has been developed by Zapffe and co-workers over the past ten or twelve years and is known as the "planar pressure theory". A succinct statement of this concept is that, "Hydrogen embrittlement is nothing other than the result of an aging action in which the precipitate is a gas", (19). An outline of the significant features of the planar pressure theory may be found in this same reference.

This theory is attractive in that it can explain many (though not all) of the observed phenomena in connection with the presence of hydrogen in steel. For example, the appearance of surface blisters in severely charged specimens seems readily explicable on the basis of the relief of internal gas pressure by the disruption of surface layers of metal. Detailed applications of the planar pressure theory of hydrogen embrittlement may be found in the literature (3, 6, 19, 26).

There are several questions pertaining to the planar pressure concept which might be raised. For one, the mosaic disjunctions or lattice rifts are of the order of magnitude of interatomic spacings in size and it is difficult to visualize the significance of the development of a high gas pressure in these voids. Admittedly, the voids increase in size as plastic flow proceeds, but it would require a very considerable enlargement to increase the volume to the point where the classical concepts of kinetic theory and gas pressure apply.

Another point to be considered is the calculation of the pressures developed by hydrogen in voids. This was first done in 1932 (38) and subsequently extended in an attempt to show that very high pressures are developed by the hydrogen present in steel. It has been pointed out (39) that these calculations give fugacity[a], and because of marked deviations from ideality at the high pressures under consideration, the true pressures would be considerably lower. Thus, the difference between fugacity and pressure may become quite considerable. At room temperature, for example, the fugacity was calculated to be approximately 2,000 times greater than the pressure at a concentration of 11 cc hydrogen/100 gm iron. The ratio, of course, diminishes as the concentration of hydrogen is decreased. However, it should be observed that even with this modification, the calculated pressure at room temperature varies from 103,000 psi to 218,500 psi for concentrations of one to eleven cc/100 gms.

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a. The ratio of fugacity to pressure is called the activity coefficient and is a measure of the deviation of a gas from ideality. For hydrogen, the fugacity may be considerably greater than the pressure.

If the planar pressure concept is correct, the precipitation of gas and subsequent embrittlement should occur in austenitic as well as in ferritic structures. It is known that the solubility of hydrogen in austenite is greater than in ferrite at the transformation temperature and this point may be used to explain the relative immunity of austenitic stainless steels to embrittlement by hydrogen. The fact remains, however, that inordinately large quantities of hydrogen are required to produce even a slight embrittlement in stainless steels.

The relationship between testing temperature and ductility provides an interesting test for the planar pressure theory. It has been shown (30, 32) that for a given charging condition the ductility first decreases, then increases, passing through a minimum as the testing temperature is increased. The first portion of the curve is readily explicable. As the temperature is increased, the diffusion of hydrogen is accelerated and precipitation in voids is facilitated. One encounters considerable difficulty in attempting to visualize how the planar pressure concepts or extensions of it might explain the minimum and subsequent increase in ductility with increasing temperature. Brown and Baldwin (32) have considered this point in some detail, and clearly demonstrated that a mechansim fundamentally different from the planar pressure theory or allied concepts must be operative under certain conditions of embrittlement.

Although the metallurgical literature on delayed failure under static load is meager, the problem has been studied in some detail in glasses. It is well known that a relatively high static load may be sustained by glass for only a relatively short time but that a lesser load may be tolerated without fracture for a much longer time. The Griffith crack theory has been employed with reasonable success in an attempt to explain this behavior (40, 41).

The concept of the presence of microcracks arose out of the large disparity between the theoretical fracture strength (based on attractive forces between atoms) and the observed fracture strengths in solids. Experimentally, it was found that theoretical strengths could be approached in some instances by prolonged annealing, by minimizing surface scratches and by testing thin fibers. Griffith (42, 43) provided a mathematical treatment for a two dimensional model which resulted in the following expression for the breaking strength of a brittle isotropic solid:

$$R = \sqrt{\frac{2\,E\,T}{\pi C}}$$

where R = stress applied normal to a crack in a thin plate

E = Young's Modulus

T = surface energy of the material,

2C = length of crack

This equation has been used by Orowan (40) to explain the phenomenon of delayed failure in glasses. The surface energy of mica was 4,500 erg/Cm^2 in vacuum and 375 erg/Cm^2 in air as determined experimentally. Since mica is chemically similar to glass, the ratio of these two values was presumed to be preserved for glasses. Referring to the Griffith formula, the ratio between strength in vacuum and strength in air should be approximately 3.5 using the above figures for surface energy. This means that two values may then be considered for R: R_v and R_a. R_v corresponds to the strength where cracks grow in a vacuum and it is relatively high, while R_a corresponds to some lower strength value where the cracks grow in an atmosphere. If a stressed specimen is exposed to a suitable atmosphere and adsorption occurs, the surface energy of the crack is reduced and the crack may then readily propagate. This propagation is limited by the fact that if a crack grows too rapidly, the vacuum value for surface energy must be considered together with the higher unit breaking stress R_v. Once crack propagation has proceeded to a point where the unit stress is greater than R_v, the crack grows rapidly and cataclysmic failure results.

Two interesting features of this concept follow. First, this would predict that there is some critical value of stress, associated with R_a, below which delayed failure should not occur. Secondly, a specimen subjected to a static load between values of the load corresponding to R_a and R_v, then subsequently unloaded short of the time necessary for failure, should have a breaking strength less than that of a specimen without the prior stress.

The work of Gurney and Pearson (41) and others (44, 45) provides experimental confirmation of this model. In one series of experiments (41) it was shown that the phenomenon of delayed failure could be eliminated by annealing glass rods in vacuum and testing them in vacuum. When tested in air, the familiar pattern of delayed failure was encountered. On the other hand, when tested in air from which both CO_2 and H_2O were removed, delayed failure was again eliminated. In those cases where delayed failure was not observed, the breaking strength of the glass rods was far above that normally obtained and approached the theoretical value.

The application of these concepts to the case of hydrogen embrittlement and delayed failure in steels has been considered (31). In the case of steels, the atmosphere adsorbed on crack surfaces would be the hydrogen present in metastable solution, and the previous reasoning could be applied. The time delay would be due to the fact that time is required for hydrogen to diffuse into the immediate vicinity of the cracks and deposit as an adsorbed layer on the growing crack surface, thereby reducing the energy of that surface.

Consideration has been given to the possibility of applying the concept of a Cottrell atmosphere surrounding a dislocation to the case of hydrogen embrittlement in steel (30, 32). This picture has been used with considerable success in explaining the yield point phenomenon and strain aging effects in steels due to the presence of carbon and nitrogen (46). The essential feature of this concept is that the presence of the interstitial solute atoms reduces the elastic strain energy in

the vicinity of a dislocation by reducing the degree of distortion. Under an applied stress, the movement of the dislocation is restrained by the atmosphere, and the dislocation may break free, remain fixed, or move through the lattice "dragging" the atmosphere with it.

In the case of hydrogen, however, little if any lattice distention has been observed with the additions of hydrogen to steel (47, 48). Furthermore, the atomic concentrations of hydrogen in steel are very low. For a steel containing 10 cc hydrogen/100 gms, the atomic percentage is 0.005 which corresponds to one atom of hydrogen for every 20,000 iron atoms. In contrast to this, a 0.1 per cent carbon steel contains 0.5 atomic percentage carbon or one carbon atom for every 200 iron atoms. Thus, the atomic concentration of hydrogen is only 1/100 that of carbon. This then, leads one to question whether a restraining Cottrell atmosphere could be formed by the solute hydrogen atoms by an elastic strain mechanism, which is considered to be the situation for nitrogen and carbon.

It has been shown (49) however, that a yield point attributable to hydrogen exists in a charged 1020 steel. The author states that, "Preliminary experiments also indicate that this yield point is not observed above about -120°C". Thus a Cottrell atmosphere due to hydrogen is presumably responsible for the yield point phenomenon. If a Cottrell atmosphere based on distortion is rejected by the size argument given above, one might consider that some other mechanism (possibly electrostatic) might be operative in reducing the energy around a dislocation.

There are certain features of similarity between the three mechanisms discussed above. In all three cases, a stress is required and the diffusion of hydrogen appears to play a significant role.

According to the planar pressure concept, as deformation proceeds, lattice rifts and mosaic disjunctions become enlarged and the diffusion of hydrogen into these voids is necessary to increase the pressure of hydrogen to the point where a reduction in flow or ductility can be accomplished. The competitive rates, then, of enlargement of voids and diffusion of hydrogen may be used to explain the decrease in ductility with increasing temperature and decreasing strain rate.

In the case of the Griffith crack concept, some flow, at least on an atomic scale, is required and the hydrogen must migrate to the region of the advancing crack. The rate of formation of new interfaces and the diffusion rate of hydrogen together with its adsorption on the new surface are to be considered.

Finally, in terms of dislocations, the restraining action of the Cottrell atmosphere may be considered to vary as follows. If the atomic mobility of hydrogen is very high, the atmosphere and dislocation may move through the lattice with relatively little drag exerted on the dislocation.[a] If atomic mobility is very low, the

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a. This device might also be used to explain the absence of a yield point due to hydrogen above some minimum temperature as found by Rogers (49).

dislocation may readily free itself from its atmosphere and proceed along its way without the drag associated with the Cottrell atmosphere. Newly generated dislocations, as from Frank-Read sources may not have the restraining atmosphere formed. Considering the movement of a dislocation and the drag which may or may not be exerted, the minimum may be rationalized in the plots of ductility vs. temperature and ductility vs. strain rate.

There are certain appealing features of each of the three theories outlined above. However, it is difficult to accept any of these mechanisms for hydrogen embrittlement without reservation. Objections to the planar pressure theory have been discussed earlier in this section. Extension of the Griffith crack theory from the case of delayed failure in glasses to delayed failure in metals seems difficult to justify because the Griffith relationship was developed for brittle materials, in terms of the stress required to separate atoms. In metals, plastic flow takes place and fracture is thought to occur by the reduction of the amount of strain a metal can exhibit. The concept of a Cottrell atmosphere might be applicable to the case of hydrogen embrittlement, but the mechanism used for explaining the atmosphere developed by carbon atoms does not seem compatible with what is known about hydrogen.

It is felt that while no one of the foregoing theories is completely acceptable, certain elements of each may be useful in explaining the various phenomena associated with the presence of hydrogen in steel. It is quite possible that combinations or modifications of these concepts will ultimately come to be accepted as the cause of hydrogen embrittlement and delayed failure in steel.

II. MATERIALS AND PROCEDURE

The material used was taken from a commercial heat of SAE-AISI 4340 steel which was furnished in 5/8" rounds 10 feet long. The chemical analysis is given in Table I. Studies were made on specimens heat treated to three different strength levels, 200,000, 230,000 and 270,000 pounds per square inch. The heat treatment consisted of austenitizing at 1550°F for 45 minutes followed by an oil quench. Tempering was accomplished by heating for one hour at 850°F, 750°F, and 450°F to give the nominal strength levels listed above. When a bainitic structure at the 230,000 psi strength level was desired, specimens were austenitized at 1550°F for 45 minutes followed by isothermal treatment at 585°F for 4 hours, oil quenched, and tempered one hour at 650°F.

Table I

COMPOSITION OF 4340 STEEL USED IN THIS INVESTIGATION

C	Mn	Si	Ni	Cr	Mo
0.39%	0.76%	0.28%	1.80%	0.75%	0.24%

The two types of specimens that were used in this work are shown in Fig. 1. An unnotched specimen, with the test section ground to a two inch radius was used for much of the tensile testing. The reduced section was carefully finished by polishing with the abrasive scratches running in the axial direction of the specimen. The sharp notch specimens were used to provide a severe stress raiser in the section under test. A 50%, 60 degree notch whose root radius was less than 0.001 inches was employed.

Blanks were cut from the as-received bar stock, normalized at 1650°F for one hour, and air cooled. They were then stress relieved by heating to 1200°F and furnace cooled. Specimens were rough machined from the blanks to 0.015 inches over the finish dimensions, heat treated as indicated above, and finish ground to the dimensions shown in Fig. 1.

Tensile testing was performed at room temperature with the crosshead feed maintained at a constant rate so that the strain rate was constant for a given specimen geometry. In those cases where a static load was applied, a dead weight horizontal lever arm type of creep rupture machine was employed. In both cases, specially designed concentric test fixtures were used to assure the highest degree of concentricity. Calibrating runs showed a maximum eccentricity of 0.001 inches.

Hydrogen was introduced by electrolytic charging where the specimen was a cathode and a cylinder of platinum gauze served as the anode of the cell. The following procedure was used almost exclusively and will be subsequently referred to as charging condition A. The specimen was first thoroughly cleaned in carbon tetrachloride. Type E specimens (unnotched) were coated with glyptal under the heads in those cases where head failures were likely to occur[a]. Specimens were charged for 5 minutes in a 4% sulfuric acid electrolyte without poison. The applied

a. Failure through the head of the unnotched specimen sometimes occurred when charged specimens, particularly at the 270,000 psi strength level, were pulled in tension. In the stress rupture tests, a high fraction of head failures occurred in charged specimens before the glyptal coating was used.

current density was 0.02 amps/per square inch. Upon completion of charging, specimens were first rinsed in water, then alcohol, and dried. Upon occasion, slight surface discoloration was observed; however, this had no noticeable effect on the test results. Those specimens which were painted with glyptal under the heads were carefully cleaned in glyptal solvent before testing, as a close fit between the specimen and holder was required in the concentric test fixtures. The time between the end of charging and beginning of a test was taken as the aging time. A five minute aging time was convenient to allow rinsing, drying and locating the specimen in the concentric test fixtures. All aging and testing was performed at room temperature.

When a more severe charging condition was desired, specimens were charged at a current density of one ampere per square inch in a 4% solution of sulfuric acid. A poison served to facilitate the entrance of hydrogen into the specimen and consisted of a solution of one gram yellow phosphorous in 20 cc of carbon disulfide. This was added to the electrolyte at the rate of 1 part to 2000 by volume.

III. RESULTS AND DISCUSSION

A. EFFECTS OF CHARGING CONDITIONS

The reduction in area at fracture in the tensile test was one of the properties which was used as an index of hydrogen embrittlement. Charging conditions were selected such that the ductility was reduced to a low value, but not zero. If the steel were embrittled to the point where fracture occurred at strains close to zero, treatments which produced improvements might be difficult to evaluate. The effects of varying the charging time, for three different strength levels, are shown in Fig. 2. The strong dependence of embrittlement on strength level is apparent. In addition, the ductility is less sensitive to charging times for the 270,000 psi strength level than for the lower strength levels.

The results of the standard charging condition A on mechanical properties are summarized in Table II for the conventional tensile test and for the sharp notch specimens tested in tension. Note that charging with hydrogen influenced the properties associated with ductility while the yield strength remained relatively unaffected. A comparison of stress-strain curves for the charged and uncharged conditions is given in Fig. 3. The only apparent effect of charging with hydrogen is to reduce the strain at fracture in the stress-strain curve.

TABLE II

EFFECT OF CHARGING CONDITION "A" ON SOME MECHANICAL PROPERTIES OF 4340 STEEL HEAT TREATED TO SEVERAL STRENGTH LEVELS

	Tempered Martensite			Bainite
Nominal Strength Level, psi	200,000	230,000	270,000	230,000
Uncharged				
Tensile Strength, psi	205,000	236,000	279,000	238,000
Yield Strength, psi[a]	195,000	220,000	235,000	210,000
Reduction in Area at Fracture, Per Cent	49	46	44	49
Fracture Strength, psi	321,000	345,000	388,000	351,000
Hardness, Rockwell C Scale[a]	43	48	53	45
Notch Tensile Strength, psi	292,000	315,000	330,000	336,000
Charging Condition "A" (5 Minute Age)				
Tensile Strength, psi	205,000	236,000	255,000	238,000
Reduction in Area at Fracture, Per Cent	36	11	3	24
Fracture Strength, psi	265,000	261,000	265,000	260,000
Notch Tensile Strength, psi	266,000	300,000	207,000	314,000

a. Yield Strength (0.2% offset) and hardness were unaffected by the charging condition used.

More severe charging conditions[a] reduced the fracture strain to values so low that it was difficult to evaluate them. It may be seen from Fig. 3 that the fracture strength serves as a more sensitive measure of the severity of embrittlement when this is the case. At the 270,000 psi strength level for example, the fracture strength could be reduced to as low as 60,000 psi or 25% of the normal uncharged yield strength, as indicated in Fig. 4. The widely different degrees of embrittlement which could be obtained by electrolytic charging are illustrated by Figs. 2 and 4.

B. EFFECT OF AGING ON DUCTILITY

A question of primary interest was the manner in which properties changed as the charged specimens were aged at room temperature. The aging time was taken as the time between the completion of charging and the beginning of testing.

The effect of aging on the recovery from the embrittled state, for three strength levels, is shown in Fig. 5. Type E specimens, after charging and aging as indicated, were tested in tension and the reduction in area at fracture was plotted as the index of embrittlement. The initial ductility (for the shortest aging times) varied inversely with strength level. On the other hand, the time for recovery did not appear to follow a consistent trend. At all strength levels, the return to full ductility as measured by reduction in area was evident after aging for 100 hours.

A curious feature of Fig. 5 should also be noted. At the 200,000 psi strength level, the ductility remained constant at 40% reduction in area for 1, 2 and 4 hours aging time, which implies the existence of a flat portion in the recovery curve. A similar behavior may be noted at the 270,000 psi strength level and again in Fig. 21.

Aging curves were determined for sharp notch specimens tested in tension. The relationship between the aging time and notch tensile strength at the 230,000 and 270,000 psi strength level is illustrated in Fig. 6. The change in notch ductility was small for the sharp notch specimens and was not as sensitive to recovery as the notch tensile strength. The latter property, then, was taken as an index of embrittlement.

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a. Charging conditions of this order have been commonly employed in studying the effects of hydrogen in steel at lower strength levels.

Certain differences in form are evident in a comparison of Fig. 6 with Fig. 5. The aging curve for the sharp notch specimens exhibited a marked minimum at approximately two hours while unnotched specimens for the corresponding strength levels showed a continuous increase in ductility. A second feature of this comparison is that the unnotched ductility has recovered to its full uncharged value by aging for 100 hours, while the notch tensile strength has not completely recovered in the same aging time. From this, one may infer that the notch test is more sensitive to the presence of hydrogen than the standard tensile test. Since charging with hydrogen may be considered as the addition of an embrittling agent to one already present, (the sharp notch) this behavior seems consistent.

C. DISTRIBUTION STUDIES

During the course of this work several instances were observed in which the fracture surfaces of charged specimens displayed a concentric ring, i.e., a change in luster across the fractured area. This has also been observed by others (6), and raised the question of how hydrogen was distributed in the test piece after charging.

Distribution studies are made difficult by the fugitive nature of hydrogen. The conventional techniques for measuring the distribution of solutes in alloys, such as in diffusion studies, seems impractical if not impossible for this particular case. Since the ductility of steels varies with hydrogen content, if only the outer layer were impregnated with hydrogen, removal of that brittle layer by machining or grinding should result in the restoration of the ductility of the specimen.

The technique consisted of charging the type E (unnotched) specimens with hydrogen and then aging at room temperature a fixed length of time. Upon expiration of the aging time, a portion of the specimen surface was removed by grinding, during which operation the specimen surface was flooded with coolant. The specimen was then finish polished and immediately tested.

The results, for three different aging times, are plotted in Fig. 7, which shows how the ductility was increased by removing surface layers from the test specimens. The abscissa is a radial distance, i.e., the thickness of metal removed from each surface. It is evident from this figure that the penetration of hydrogen into the test specimen during charging must have been relatively small, as the removal of the outer 0.020 inches of surface permitted the return to full ductility at the shortest aging time. Upon aging, as indicated in Fig. 7, the embrittled zone was displaced inward.

An interesting feature of the relationships shown in Fig. 7 is that specimens aged four hours exhibited a considerably greater depth of the embrittled zone than specimens aged five minutes. This was true despite the fact that the charged ductility (without removal of stock) after aging four hours was greater than after aging five minutes. Thus, it is evident that two factors are operative; one, the depth of embrittlement and two, the degree or severity of embrittlement.

A comparison of the hydrogen distribution for two different strength levels at an aging time of five minutes is presented in Fig. 8. The same amount of hydrogen, (identical charging conditions) and the same depth of embrittlement penetration have a more deleterious effect on steel treated to a 270,000 psi strength level than at a 230,000 psi strength level.

It is significant that the relatively shallow brittle zone of less than 0.020 inches was sufficient to cause a substantial decrease in ductility. Similar behavior has been observed in steels which have been carburized, siliconized, or nitrided. It appears then that hydrogen may have certain features in common with other solute elements when a brittle surface layer is formed.

This work clearly demonstrates the vital role played by the distribution of hydrogen. Delayed failure, loss of ductility, etc., all were caused by the shallow layer of hydrogen at the surface, and a high concentration of hydrogen throughout the specimen was not necessary to produce these phenomena.

D. DELAYED FAILURE STUDIES (5 MINUTE AGING TIME)

The primary objective of this work was to study the phenomenon of delayed failure and its relationship to hydrogen embrittlement. Sharp notch specimens (Type J) were used in order to localize the region of fracture and to provide a multiaxial stress state. The data presented in Fig. 9 show that delayed failure will occur in steels charged with hydrogen.

One of the striking features of these relationships is the relatively low applied stresses that were sufficient to produce delayed failure. When compared with the yield strengths given in Table II, it may be seen that applied stresses of as little as 40% of the yield strength[a] (270,000 psi strength level) can cause

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a. This does not mean to imply that there is no flow, since the unit stress at the root of the notch is considerably greater than the applied stress. This will be considered in detail later.

failure in several hours. Identical notched specimens in the uncharged condition were stressed at high loads as indicated in Fig. 9 and remained unbroken after times of over 250 hours.

Regardless of the strength level, the times to failure were all of the same order of magnitude, and extended roughly over one log cycle. Within a given strength level, there seemed to be only a slight dependence of failure time on the applied stress. Thus, the delay in time for failure is evidently independent of strength level and only slightly dependent upon applied stress for the particular set of test conditions employed. Varying the test conditions may alter the relationships cited. Since the mobility of hydrogen is a factor which may be expected to remain approximately independent of the strength level and applied stress, the time to failure appears to be associated with the diffusion of hydrogen, which may well represent the time to accomplish a redistribution of hydrogen.

The plateau of the stress-rupture curves at high applied stresses coincided with the notch tensile strength for a given strength level. It seems axiomatic that if a static load were applied which was in excess of this value, failure would occur on loading. In those cases where this was tested by applying static loads just above and below the value of the notch tensile strength, the correlation was justified. It should be noted, however, that the tensile test represents continuously increasing applied loads over a finite period of time, and as such, may mask short delayed failure times. The upper critical stress value at the 270,000 psi strength level was less than that of the other two strength levels. Presumably this is due to the fact that the embrittlement caused by hydrogen was sufficient to give the marked decrease in notch strength observed at the 270,000 psi strength level.

A most significant characteristic of the stress-rupture relationships is the fact that there was a minimum critical value of applied stress below which delayed failure did not occur.[a] It is evident that for a sharp notch specimen an externally applied stress gives a high localized stress concentration. By exceeding some minimum value of applied stress, the unit stress at the root of the notch is high and may well be sufficient to cause plastic flow and subsequent failure.

E. EFFECT OF NOTCH ACUITY ON STRESS RUPTURE TESTS

The dependence of the minimum critical stress for delayed failure upon the necessity for plastic flow may be tested by varying the notch acuity. A specimen

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a. The static load was discontinued if a specimen remained unbroken after 100 hours.

with a milder notch should require a higher applied stress to produce plastic flow at the root of the notch and thus exhibit a higher minimum critical stress to produce delayed failure. The radius at the root of the notch was increased to 1/32 inch and also to 2 inches, while the 50% notch depth was held constant. Fig. 10 is a comparison of stress-rupture curves for specimens at the 230,000 psi strength level with three different notch sharpnesses. It is immediately apparent that the lower critical stress value was raised as the notch acuity was decreased.

A similar comparison was made at the 270,000 psi strength level by making stress rupture tests on 2 inch radius specimens, as summarized in Table III. Again, failure took place either immediately or not at all, depending upon the applied stress. The critical stress, in this case 225,000 psi falls between the yield point and proportional limit of the material (cf. Fig. 3 and Table II).

TABLE III

STRESS RUPTURE TESTS ON CHARGED 2" RADIUS SPECIMENS AT THE 270,000 PSI STRENGTH LEVEL

Applied Stress psi	Time to Fracture Hours	Reduction in Area at Fracture -- %
240,000	0.3	2.3
230,000	0.2	2.9
230,000	0.55	2.3
220,000	Unbroken - 140 hours	-
220,000	Unbroken - 236 hours	-
200,000	Unbroken - 146 hours	-
200,000	1.6	a

a. Fracture occurred away from minimum section. See Text.

An interesting set of relationships may be developed by a comparison of the upper and lower critical stress values given in Fig. 10. As the notch acuity was increased, the spread between the upper and lower critical stress values also increased and the ratio between the two is summarized in Table IV[a].

TABLE IV

COMPARISON OF CRITICAL LOAD VALUES IN STRESS RUPTURE TESTS

(Data from Fig. 10)

Notch Radius	Notch Tensile Strength - psi (A)	Minimum Critical Stress For Delayed Failure - psi (B)	Ratio A/B
<0.001"	300,000	120,000	2.5
1/32"	270,000	165,000	1.6
2"	220,000	215,000	1.0

The necessity for exceeding some critical stress value to produce delayed failure has been clearly demonstrated by varying the notch acuity of the test specimen. For the sharp notch, with the highest degree of stress concentration, delayed failure was produced by the smallest load. The milder notch (1/32" radius) required a greater applied stress for flow at the root of the notch to take place. In the 2 inch radius specimen any stress concentration was very slight so that plastic flow occurred in the entire section rather than at localized regions.

However, in some abnormal cases fracture occurred at a point removed from the minimum section of the test piece (Table III), while in other instances, fracture took place under the head of the specimen at the 0.030 inch fillet. Some cases were even observed where the delayed failure took place in the 0.300 inch

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a. These ratios closely match the stress concentration factors for the respective notch geometries, although the physical significance of the ratio is not apparent.

diameter section of the specimen (Fig. 1). This was traced to the presence of almost imperceptible circumferential grinding scratches and the seemingly anomolous behavior is readily understandable in the light of the discussion on the effect of stress raisers in the presence of hydrogen.

F. EFFECT OF AGING TIME ON STRESS RUPTURE TESTS

Since the embrittlement characteristics of steel show a strong dependence on aging, the effect of varying the room temperature aging time before applying a static load was examined. The experimental procedure was to charge with hydrogen, age various times at room temperature, then apply a static load until failure.

At the 230,000 psi strength level (Fig. 11), the time to fracture was plotted as a function of the aging time for several values of applied stress. Note that these curves are of the same form as the aging curves previously discussed. At low values of applied stress, the sensitivity to delayed failure was lost in less than an hour, while for higher stresses, delayed failure occurred in specimens aged for a considerably longer time.

The same relationship may be examined by determining stress-rupture curves for various aging times. This approach was employed in studies at the 270,000 psi strength level, see Figs. 12 and 13. The stress dependence of time to failure was previously noted to be small for the five minute aging time, but at longer aging times (48 to 96 hours) a rather strong dependence was observed.

It is instructive to present the relationships between aging time, applied stress and time to failure on a three-dimensional graph. The data of Figs. 11, 12 and 13 are so treated in Figs. 14 and 15.

Aging 100 hours at room temperature subsequent to charging did not eliminate the phenomenon of delayed failure. However, after the same aging time of 100 hours, the reduction in area has recovered to its full uncharged value (Fig. 5). This means then, that delayed failure may occur in a high strength steel which exhibits full ductility as determined by conventional tensile tests. Hence a normal value of reduction in area is no guarantee that delayed failure cannot occur. On the other hand, the notch tensile strength after an aging period of 100 hours still fell short of the uncharged value (Fig. 6) and may be a better measure of the recovery insofar as delayed failure is concerned.

The lower critical stress below which delayed failure did not occur, increased continuously with aging time. It is evident in both Figs. 14 and 15 that at

longer times this value must increase quite rapidly.

G. AGING WITH AND WITHOUT APPLIED STRESS

Further examination of the stress rupture data broadens the picture of the role of flow which has already been considered in the discussion of the effects of notch acuity. In the delayed failure curves previously presented (Fig. 9, for example), it is evident that the time to failure is essentially aging time under load. This may be considered analogous to the aging curves for sharp notch specimens (as in Fig. 6) except for the fact that it is impossible to get data for times beyond the (minimum) inflection point, as the specimen would fracture.

In order to determine the influence of aging under load on the recovery of ductility, unnotched tensile specimens were aged for various times at an applied stress of 200,000 psi, then subjected to conventional tensile tests. There was no apparent difference in the reduction in area in the tensile test between specimens aged without load and those aged at a stress of 200,000 psi (Fig. 16). The applied stress of 200,000 psi was not capable of producing the minimum amount of plastic deformation which was required, since failure under static load did not occur. (Cf. Fig. 10).

Consider, however, the behavior of notched specimens at the 270,000 psi strength level as shown in Fig. 17. Aging at a stress of 140,000 psi, which was sufficient to produce delayed failure (Fig. 9) lowered the notch tensile strength below the value obtained by aging without load. This stress applied during aging was in excess of the critical value of stress associated with flow at the root of the notch. If a line is drawn through the three solid points (aged at 140,000 psi) and extrapolated to short times, it tends toward convergence with an extension of the curve for aging without load. The increment of embrittlement, due to aging at a stress value in excess of the lower critical stress, increases as the aging time under load is prolonged.

At the applied stress of 140,000 psi failure resulted in several hours aging time. Longer aging times under load were attained at a stress below the lower critical value, this is also shown in Fig. 17. It is apparent that once again there is no difference between aging without load and aging at some stress, below a critical value, which is presumably associated with the initiation of plastic flow.

Further experiments were conducted in which specimens were aged alternately without load and at a stress in excess of the lower critical value. This is illustrated schematically in Fig. 18, for five different aging treatments. In all cases the specimens were charged, aged at no load, then a static stress of 160,000

psi was applied for the times indicated. Note that the applied stress of 160,000 psi is greater than the lower critical value of stress for the five minute aging time (Fig. 9).

In the first case (A), the conventional stress rupture test after a 3.6 hour aging period at no load, the specimen remained unbroken after 94 hours at an applied stress of 160,000 psi. Here the 3.6 hour age was sufficient to raise the lower critical stress value above the static stress which was applied, and the specimen did not break. In the second case (B), the load was immediately applied for 0.1 hours, then released for 3.5 hours. The specimen subsequently broke after aging 2.8 hours at the applied stress of 160,000 psi. This behavior illustrates the significance of the increase in the lower critical stress value with aging time at no load. These two treatments also confirm the deleterious effects of even a short time age at a stress greater than the lower critical stress value.

If a specimen was stressed at 160,000 psi for only 0.1 hours, aged at no load for 100 hours and subsequently subjected to the stress rupture test, delayed failure at an applied stress of 160,000 psi was not observed after 69 hours (Fig. 18, (C)).[a] If the initial aging under load was carried out for 3.5 hours (just short of failure) and then aged without load for 100 hours, the time to failure after reloading was 0.9 hours (D). The total time at load in this latter case was 4.4 hours while the total aging time after charging was 104.5 hours.

This behavior may be rationalized in terms of the observations on aging with and without load (Fig. 17). There appeared to be only a slight difference between aging with and without load for the short time period of 0.1 hours according to the previous observations (Fig. 17). This was confirmed in Fig. 18, (C), by the fact that the brief initial aging treatment under load had no apparent effect on the stress rupture behavior (at 160,000 psi) after aging 100 hours without load. However, the fact that the notch tensile strength still exhibited a significant lack of recovery would lead one to believe that a higher applied stress, after aging 100 hours at no load, would have caused delayed failure. In the treatment (D) where the load was first applied for 3.5 hours, the effect of aging under load was severe enough to inhibit the loss of embrittlement (as measured by the stress-rupture test) after aging for 100 hours at no load.

The final treatment, Fig. 18 (E) consisted simply of cyclic aging between no load and an applied stress of 160,000 psi. The total elapsed time to failure was identical with that of treatment B.

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a. The specimen was tested after aging an additional 800 hours at no load and had a notch tensile strength of 275,000 psi. This is substantially below the uncharged notch tensile strength as shown in Fig. 6 (230,000 psi strength level).

Instead of aging at no load, other experiments were performed in which specimens were aged at applied stresses above and below the lower critical stress value. As illustrated in Fig. 19, three specimens were stressed 0.1 hours at 175,000 psi (above the critical stress), then aged 100 hours at 60,000 psi (below the critical stress value). The applied stress was then increased to the various values indicated. The initial treatment at 175,000 psi was sufficient to cause failure on loading to 250,000 psi (A), while in the second case (B) a stress of 225,000 psi was sustained 1.65 hours after the initial treatment. In the third case, Fig. 19 (C), the static stress of 200,000 psi was not sufficient to produce delayed failure in 165 hours. The stress was increased to 225,000 psi for 31 hours then broke on loading to 235,000 psi.

The aging treatments described in Figs. 18 and 19 vividly demonstrate the significance of aging above and below the lower critical stress value. This also makes possible a qualitative understanding of the wide range in times to failure reported in the field. For the charging conditions employed in this work, failure times have been observed which range from several minutes to several hundred hours between charging and failure.

H. BAINITIC STRUCTURES

One might raise a question regarding the role of retained austenite when considering the phenomenon of delayed failure in martensitic steels. Some small amounts of retained austenite may be present and, under the influence of an applied static stress, transform with a resultant localized stress sufficient to cause delayed failure. The greater solubility of hydrogen in austenite would give a non-uniform distribution of hydrogen on transformation.

A bainitic structure[a] heat treated to 230,000 psi was produced for comparison with tempered martensite heat treated to the same strength level. The charged specimens with a bainitic structure followed basically the same behavior as the tempered martensite (Fig. 20), and was displaced slightly upward when compared with the tempered martensite. This displacement may be attributed to the fact that the residual stress state in an austempered structure is inherently less severe than that of a quenched and tempered structure. In other words the martensite,

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a. An X-ray diffraction pattern of this bainitic structure showed no trace of retained austenite. The sensitivity of the technique was estimated to be sufficient to detect the presence of less than 1% retained austenite if it were present.

with its higher residual stress state, required a smaller externally applied stress to cause delayed failure.

The room temperature aging characteristics of specimens with a bainitic structure are shown in Fig. 21. Again, the corresponding curve for tempered martensite has been superimposed. It is immediately apparent that the initial embrittlement is less severe for the bainite than for the martensite. In specimens with a bainitic structure, the recovery of ductility with aging time appeared markedly slower than the recovery of ductility for specimens with a tempered martensite structure.

J. EVALUATION OF VARIABLES

One of the difficulties encountered in this work was the sporadic occurrence of scatter in the experimental data. This has been observed by others, and in some instances electrolytic charging has been abandoned in favor of thermal charging for this and other reasons.

One source of variation might be in the chemistry of the steel itself. Zapffe and Haslem (13) for example, found two different charging curves (plot of bend angle vs. charging time) for specimens taken from the two ends of a 50 foot coil of wire. Both chemical and metallographic analyses yielded no clue to the origin of this difference. A somewhat similar behavior was observed in this study and is shown in Fig. 22. The only difference between the curves is that one was displaced some 75,000 psi with respect to the other. The two series of specimens came from the same bar, but each series was prepared separately. This means that each group of specimens was rough machined, heat treated and finish ground at one time. It is apparent that despite all the precautions to maintain uniformity between batches, some factor was different and gave the behavior observed in Fig. 22. The two curves, however, are internally consistent.

Since a relatively mild charging condition was used, it was not particularly surprising that erratic results might be obtained if suitable precautions were not taken. There are many factors which could affect the amount of hydrogen absorbed by the specimen; the obvious variables, current density, charging time, bath temperature, etc., were readily controllable. Every attempt was made to prevent the entrance of impurities into the electrolyte, as the presence of only minute amounts of substances which act as a "poison" would be sufficient to alter substantially the quantity of hydrogen absorbed by the specimen. Oil in fillets, finger prints, lubricant in the centering holes, etc., all were carefully removed before charging.

The specimen preparation was another factor which had to be carefully controlled. A case has been cited in connection with Table V, where an apparently polished surface showed delayed failure away from the minimum section. This was subsequently traced to almost imperceptible circumferential scratches which had not been removed in the final polishing operation.

There are other factors which might affect the behavior of charged specimens during the aging and testing period. In one or two cases where the specimen oxidized, presumably due to electrolyte not completely removed from the root of the notch, an erratic point was obtained in the stress rupture test. The strain rate, aging temperature and testing temperature are also variables which could affect the results but which were held constant.

The heat treating operation is another source of variation. Perhaps the most difficult variables to evaluate would be associated with the quenching operation, where any cooling rate greater than the critical cooling velocity would yield the same structure and the same properties by most testing standards. However, a considerable difference may exist in the residual stress state after quenching, and this might be manifest in some test such as the stress rupture tests performed here. The behavior reported in Fig. 22 is a case in point. The specimens from which the lower curve was obtained may have had a more severe concentration of residual stress than the specimens from which the upper curve was determined. In other words, the specimens were in essence preloaded and required a smaller applied stress to give delayed failure. This concept is further strengthened by the observations reported for specimens with a bainitic structure (Fig. 20). The upper curve then, gives a more nearly correct picture of the effect of an externally applied stress on time to failure, and was used previously in Fig. 9.

It was felt that the scatter encountered in this work did not have any serious effect on the validity of the data reported. It simply meant that care and judgment had to be exercised in the acceptance of data taken from each batch of specimens.

IV. SUMMARY AND CONCLUSIONS

Each of the three theoretical concepts discussed in the introduction might be capable of explaining the observations reported. The questionable features of each theory have already been pointed out, but a model similar to that used in the Griffith crack concept is attractive, particularly when considering the data on delayed failure. The strong similarity between data obtained for glasses and steel is striking, and Fig. 23 has been reproduced from Gurney and Pearson (41) to illustrate this. The dashed curve has been added by the present authors, and the essential features of the stress-rupture curves as determined for steel are

evident in this interpretation of the data. A hydrogen charged steel would correspond to glass in the atmosphere and uncharged steel would be comparable to glass tested in vacuum. Thus, the upper and lower critical stress values of the stress rupture test and the observed effects of aging with and without load would seem readily explicable by following the same line of argument as given for glass.

In summarizing, the foregoing work has resulted in the opening of three avenues of approach to the study of delayed failure and the presence of hydrogen in steel. Stress rupture curves have been determined and the effects of strength level, notch acuity and aging time at room temperature were considered. The patterns of the effects of these major variables have been established. The distribution studies are particularly interesting because they show that the distribution of hydrogen in steel is of major importance and that a small amount of hydrogen distributed in a certain way can produce drastic embrittling effects. Studies on aging with and without load, together with varying the notch acuity, have helped to clarify the role of plastic flow in delayed failure and hydrogen embrittlement.

As a result of the foregoing experimental work, a number of conclusions may be drawn:

1. Brittle delayed failure at relatively low applied stresses can be made to occur in steels electrolytically charged with hydrogen.

2. The sensitivity to delayed failure may persist after aging long enough for "full recovery" as measured by the reduction in area in tensile testing. Under certain conditions, the notch tensile strength may be a better index of the recovery.

3. Delayed failure under static load is attributed to the application of some minimum critical amount of stress in the presence of hydrogen. If stressed below this critical value, delayed failure will not occur.

4. Distribution studies have shown that there are two factors to consider, one the depth of hydrogen penetration and two, an intensity factor or the degree of embrittlement, associated with concentration.

5. The effects of aging under load depend upon the magnitude of the load. If the applied stress is above some critical value, cumulative permanent damage occurs. If below the critical value, there appears to be no difference between aging with and without load.

6. Delayed failure occurs in the absence of retained austenite and therefore cannot be attributed to austenite decomposition.

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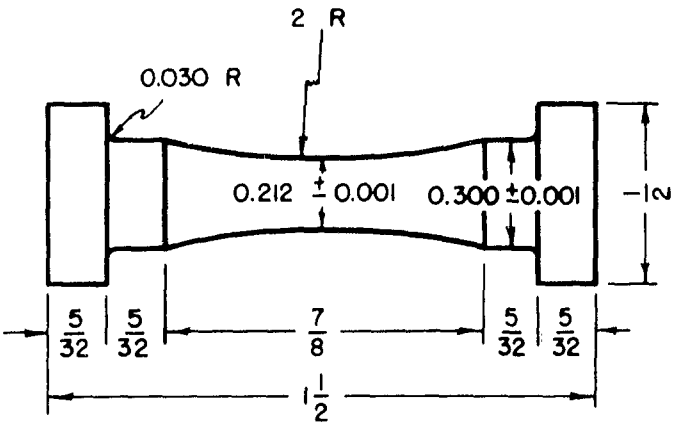
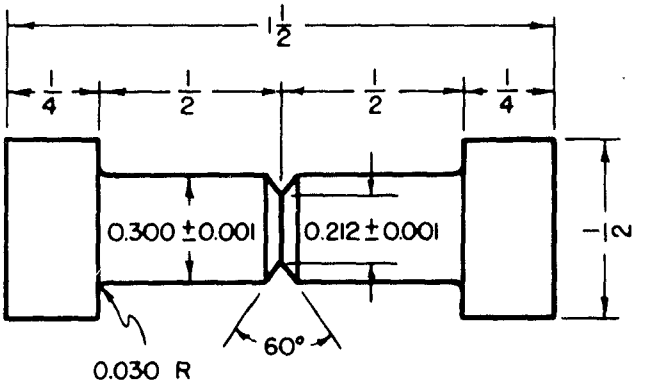


UNNOTCHED TENSILE SPECIMEN (TYPE E)



NOTCHED TENSILE SPECIMEN (TYPE J)

FIG. 1 : SPECIMEN TYPES USED IN THIS INVESTIGATION.

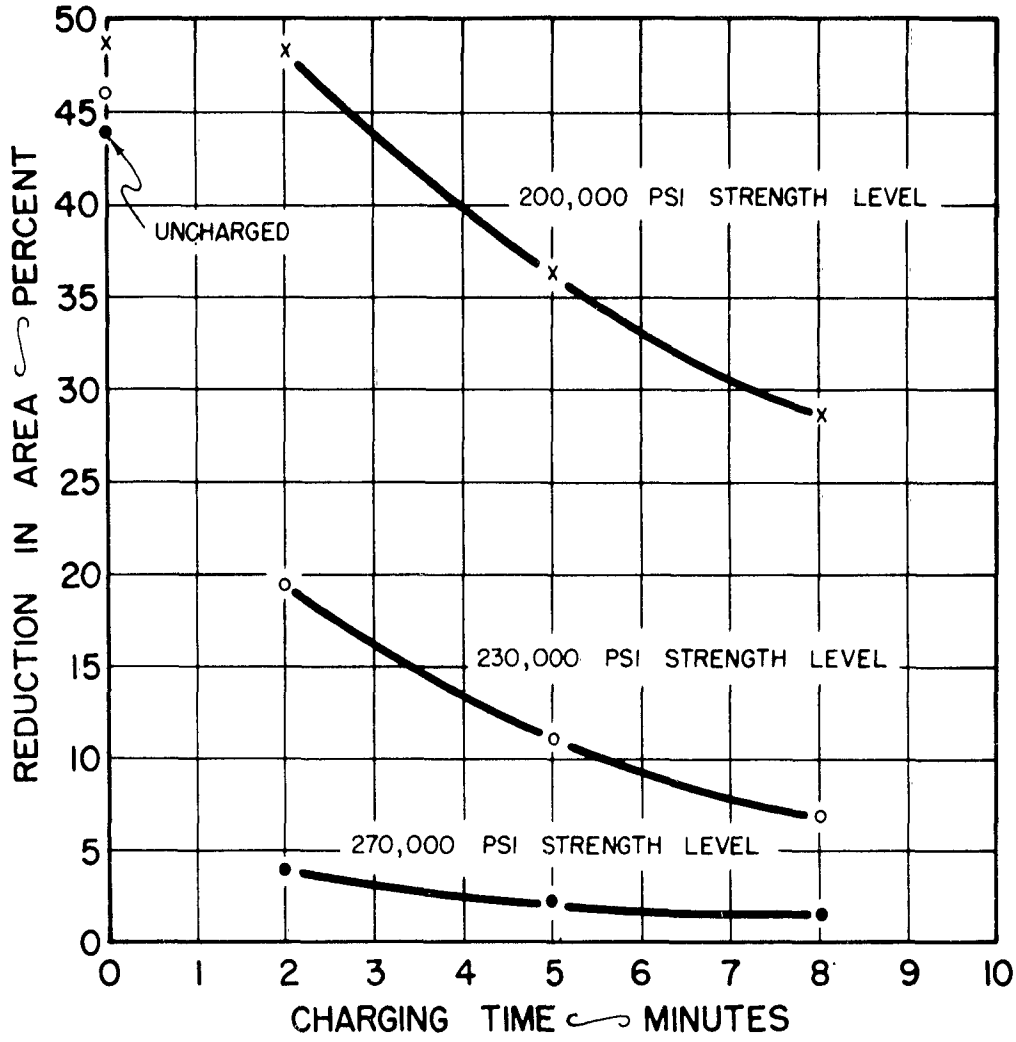


FIG. 2 : EFFECT OF CHARGING TIME ON DUCTILITY OF 4340 STEEL HEAT TREATED TO VARIOUS STRENGTH LEVELS (4% H_2SO_4, 0.02 AMPS/SQ. IN. AGED 5 MINUTES AT ROOM TEMPERATURE BEFORE TENSILE TESTING)

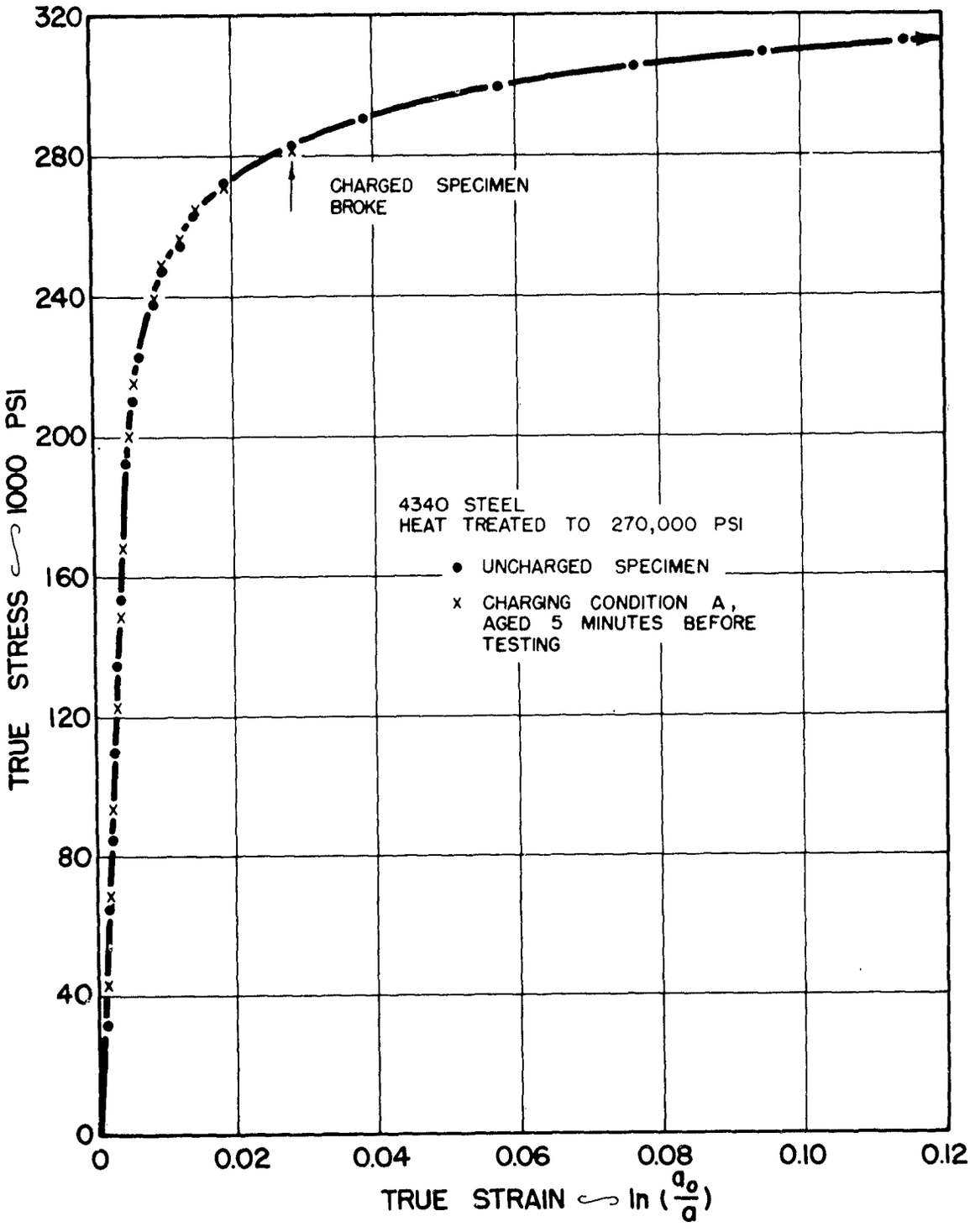


FIG. 3: INITIAL PORTION OF TRUE STRESS – TRUE STRAIN CURVE FOR CHARGED AND UNCHARGED SPECIMENS.

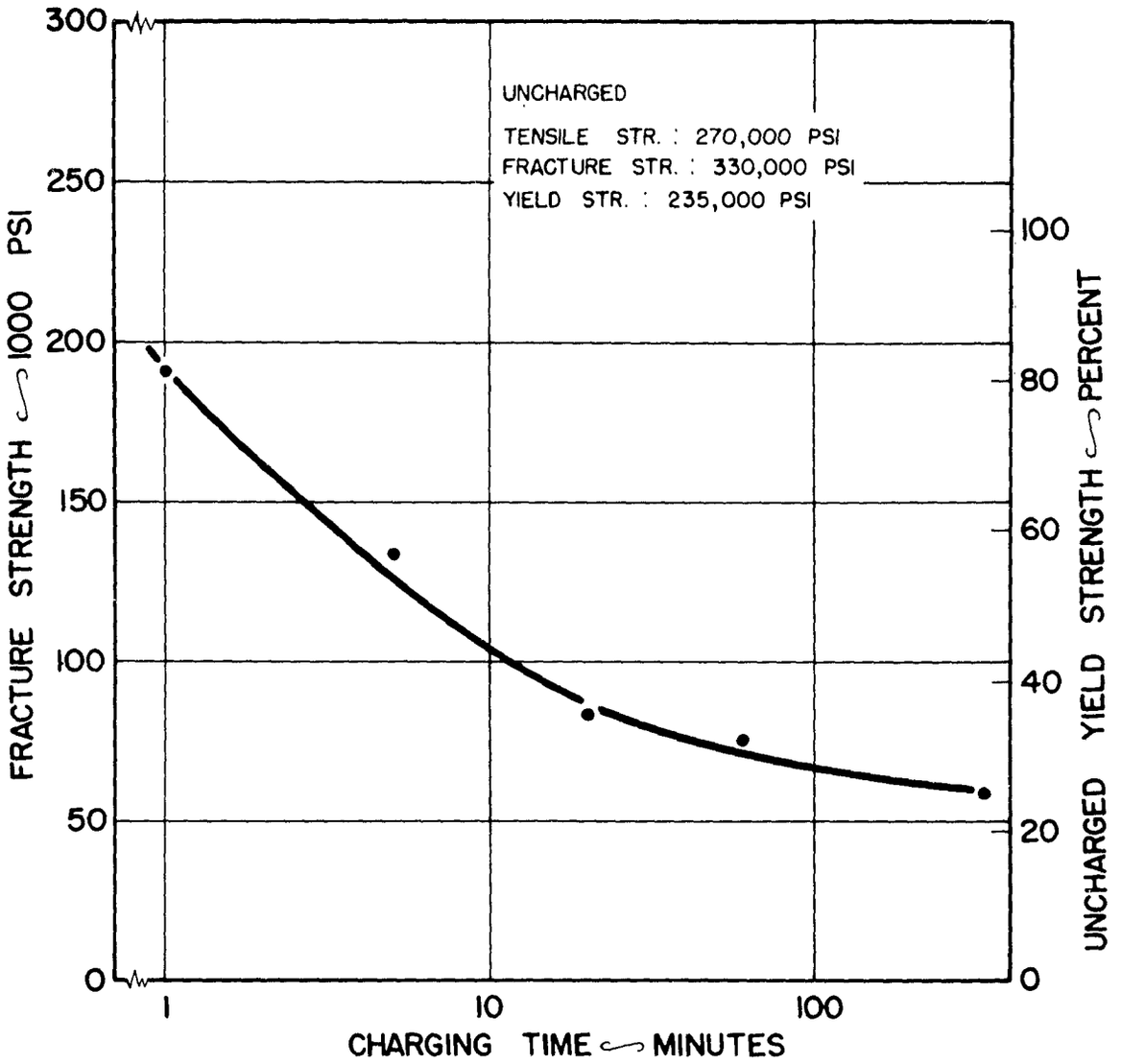


FIG. 4: EFFECT OF CHARGING TIME ON STRENGTH OF 4340 STEEL AT THE 270,000 PSI STRENGTH LEVEL. (4% H_2SO_4, 1 AMP / SQ. INCH, POISON ADDED. AGED FIVE MINUTES AT ROOM TEMPERATURE BEFORE TESTING)

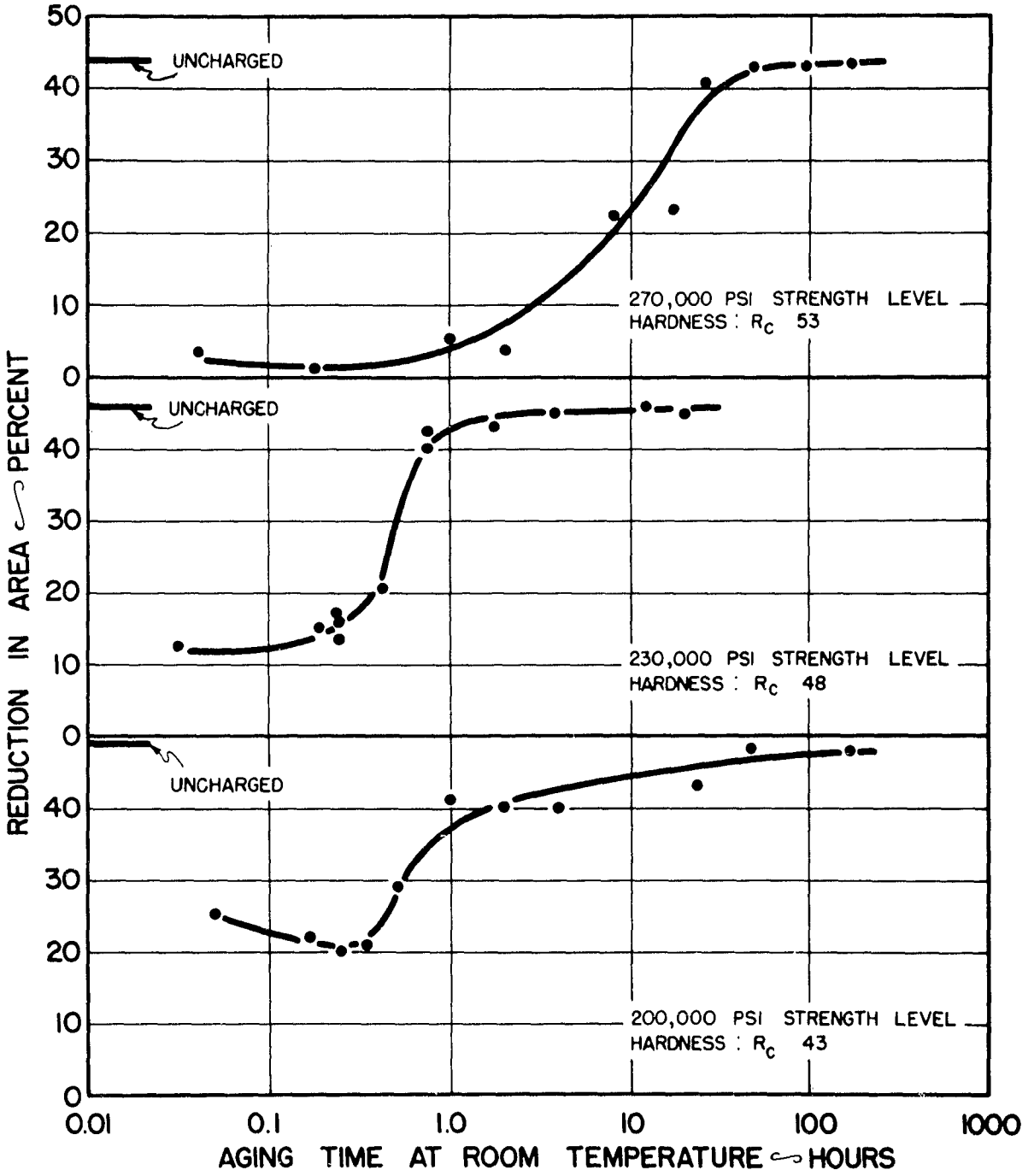


FIG. 5: EFFECT OF AGING TIME ON DUCTILITY OF 4340 STEEL HEAT TREATED TO SEVERAL STRENGTH LEVELS. (UNNOTCHED TENSILE TESTS, CHARGING CONDITION A)

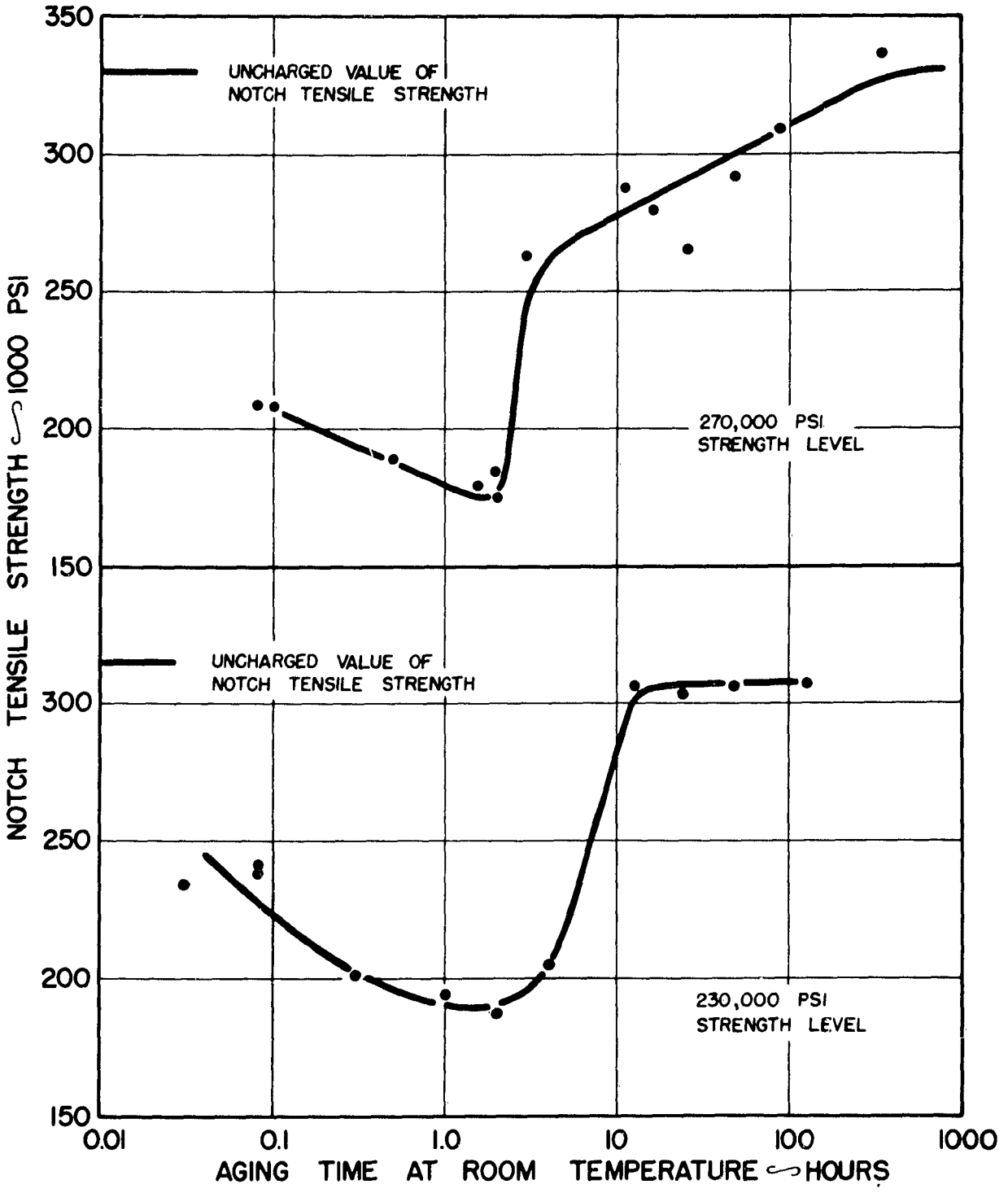


FIG. 6: EFFECT OF AGING TIME ON NOTCH TENSILE STRENGTH OF 4340 STEEL HEAT TREATED TO TWO STRENGTH LEVELS. (CHARGING CONDITION A)

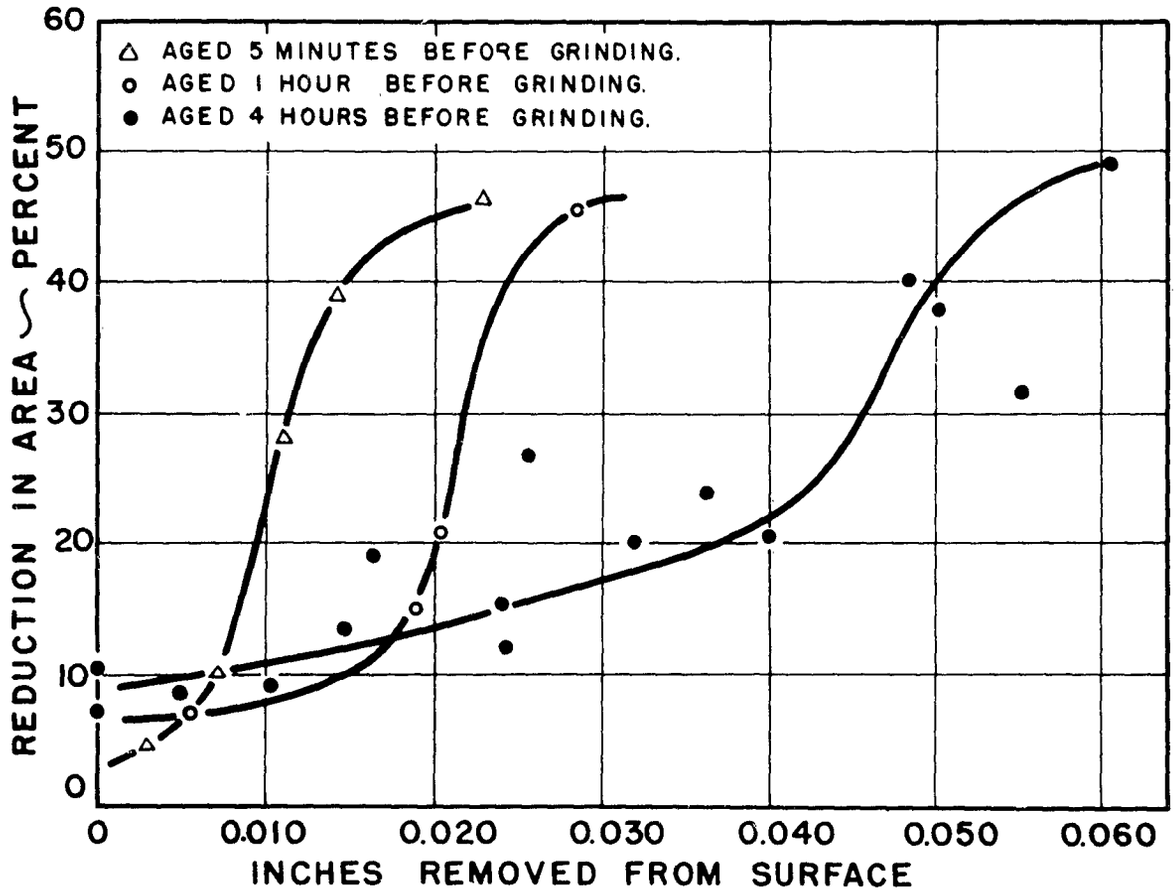


FIG. 7: EFFECT OF REMOVING SURFACE LAYERS OF METAL FROM CHARGED SPECIMENS. UNNOTCHED TENSILE SPECIMENS, 270,000 PSI. STRENGTH LEVEL, CHARGING CONDITION A, AGED AS INDICATED.

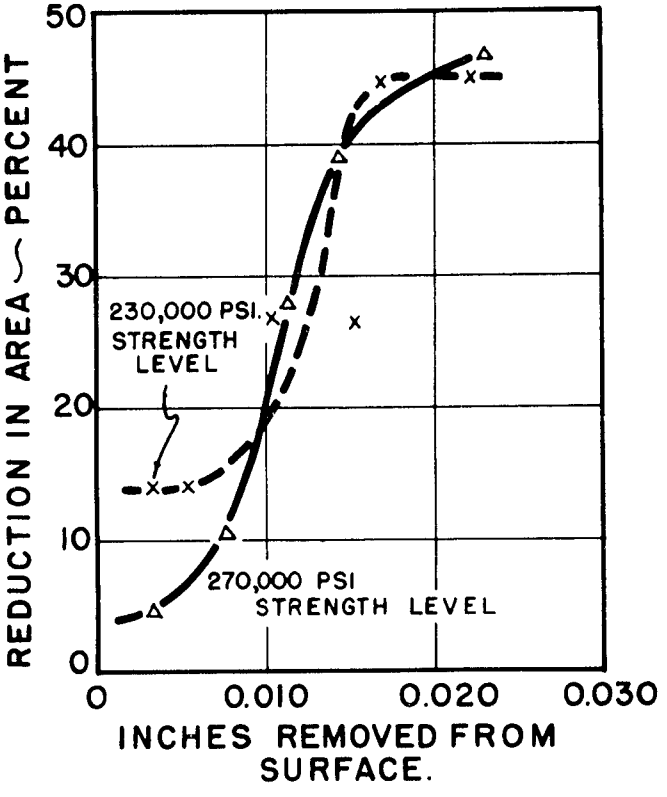


FIG. 8: EFFECT OF REMOVING SURFACE LAYERS OF METAL FROM CHARGED SPECIMENS HEAT TREATED TO TWO DIFFERENT STRENGTH LEVELS. UNNOTCHED TENSILE SPECIMENS, AGED FIVE MINUTES BEFORE GRINDING. (CHARGING CONDITION A).

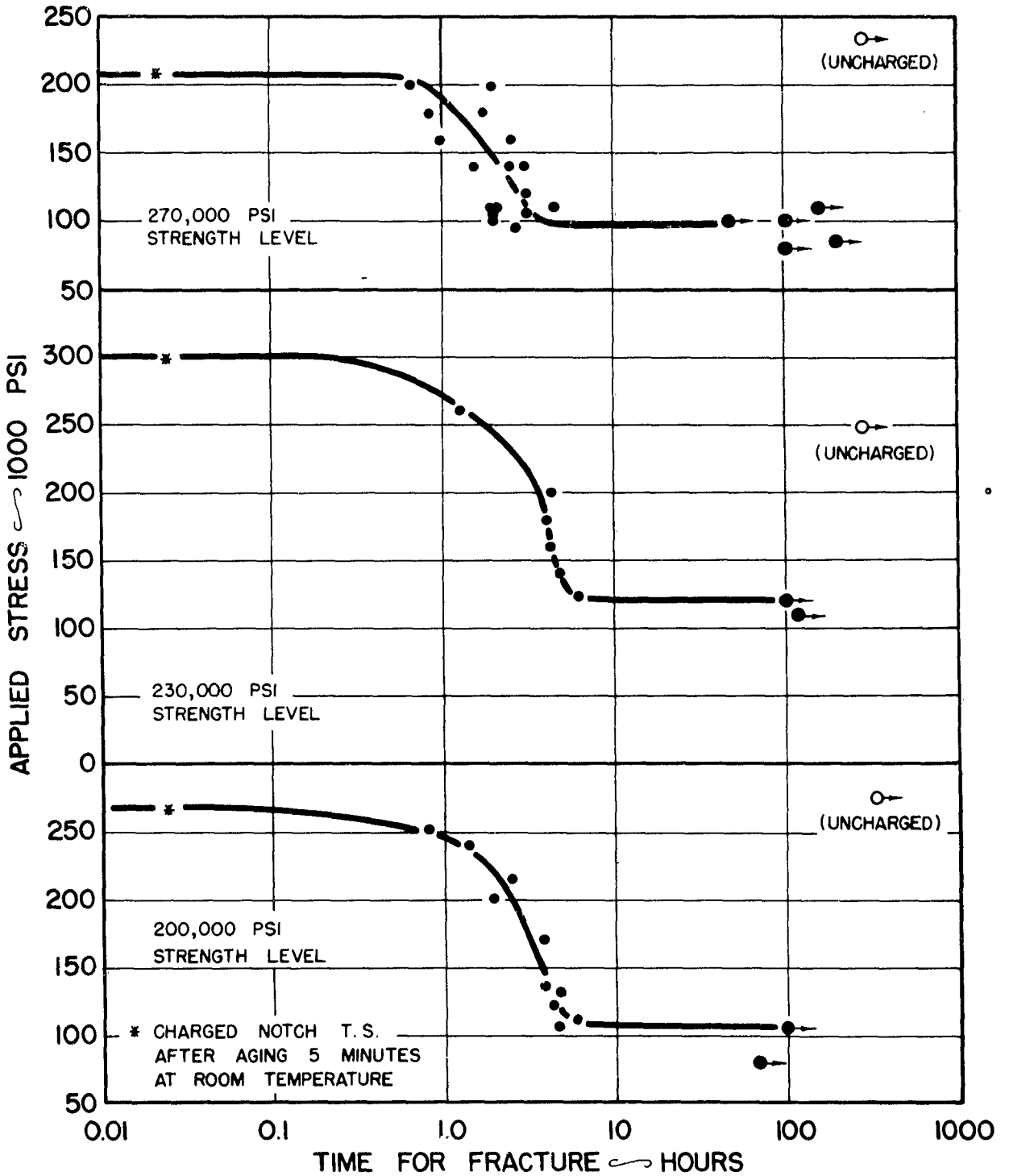


FIG. 9: STRESS RUPTURE TESTS ON 4340 STEEL HEAT TREATED TO SEVERAL STRENGTH LEVELS. (CHARGING CONDITION A, AGED FIVE MINUTES, SHARP NOTCH SPECIMENS)

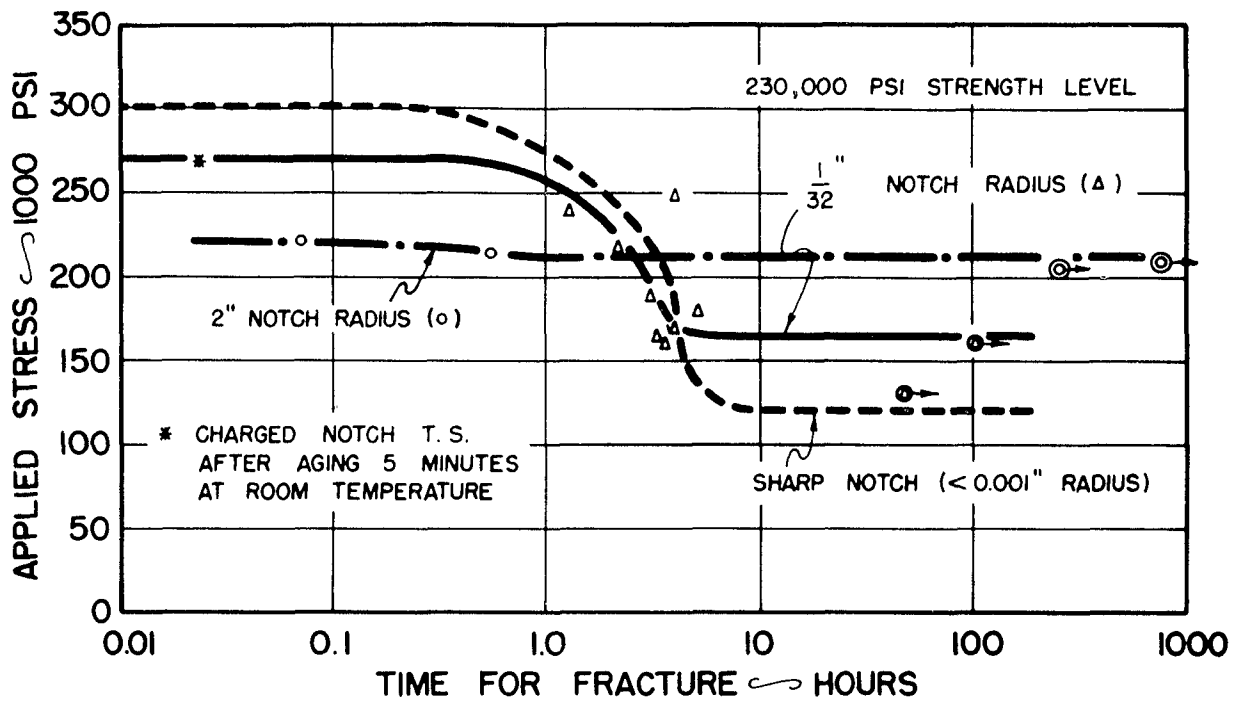


FIG. 10: COMPARISON OF STRESS RUPTURE PROPERTIES FOR SPECIMENS OF DIFFERENT NOTCH SHARPNESSES. (CHARGING CONDITION A, AGED FIVE MINUTES)

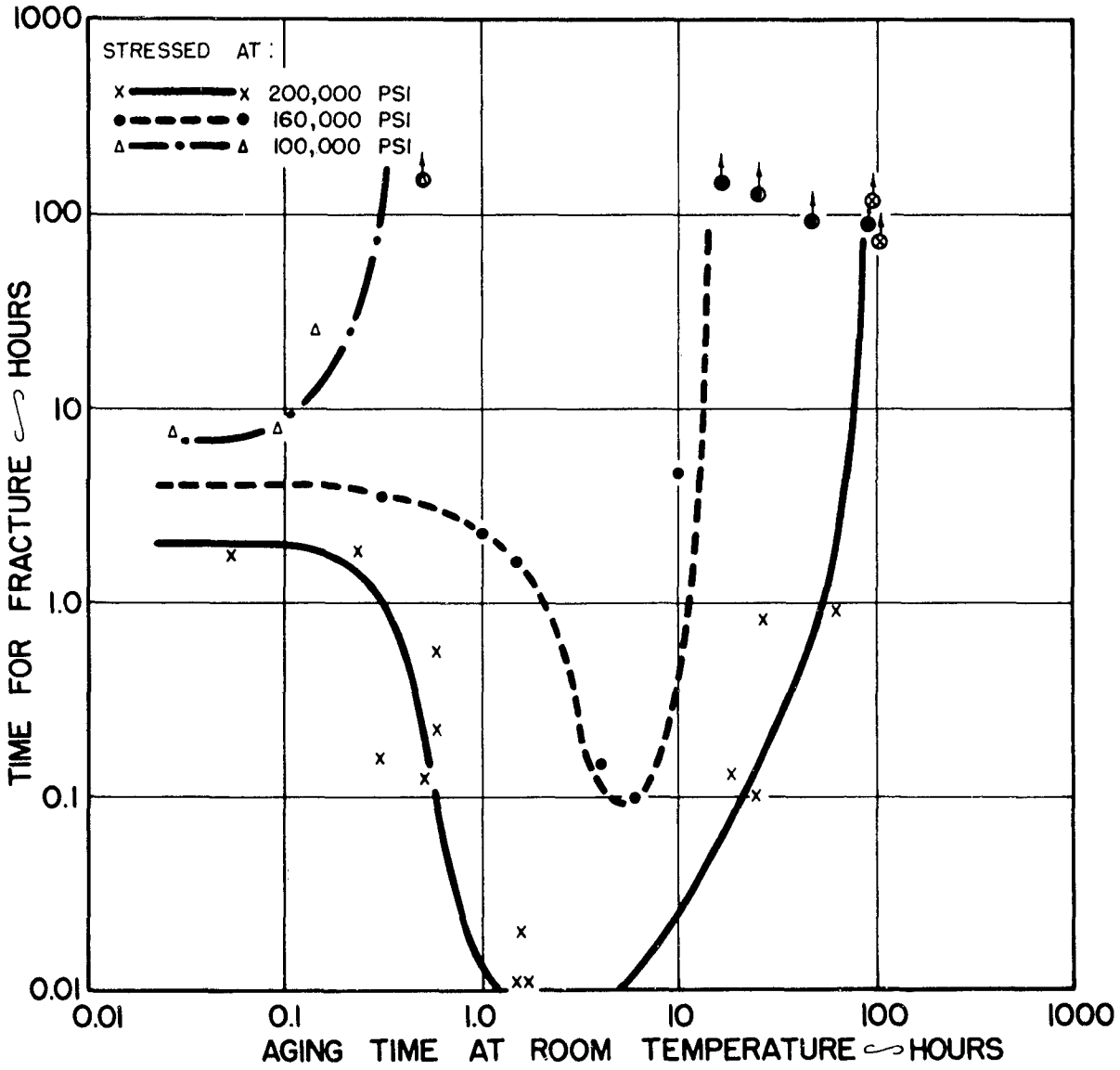


FIG.11 : EFFECT OF AGING TIME AT ROOM TEMPERATURE ON TIME TO FRACTURE FOR 4340 STEEL HEAT TREATED TO 230,000 PSI (CHARGING CONDITION A, SHARP NOTCH SPECIMENS)

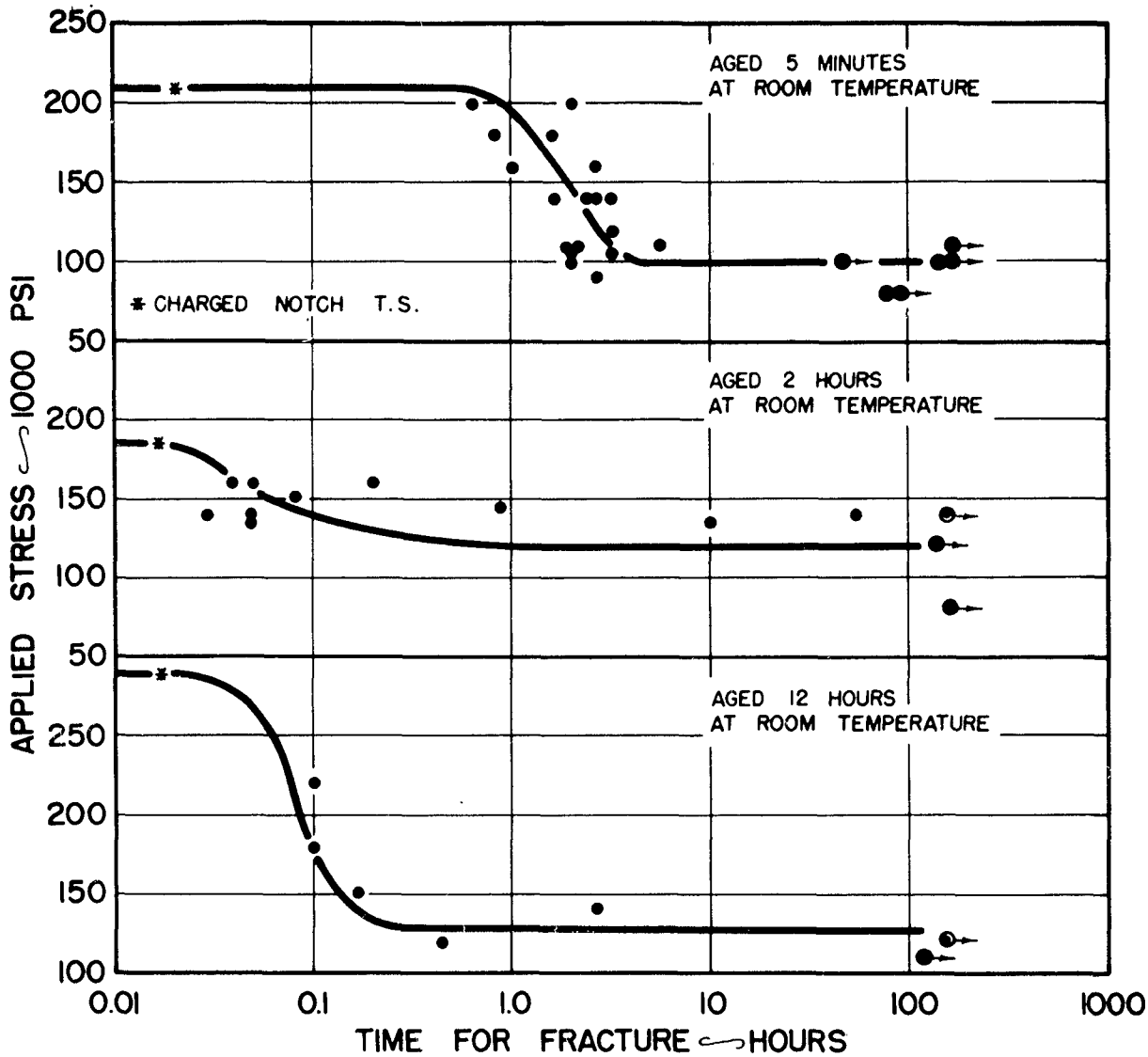


FIG. 12: STRESS RUPTURE TESTS ON 4340 STEEL HEAT TREATED TO 270,000 PSI AND AGED AS INDICATED. (CHARGING CONDITION A, SHARP NOTCH SPECIMENS)

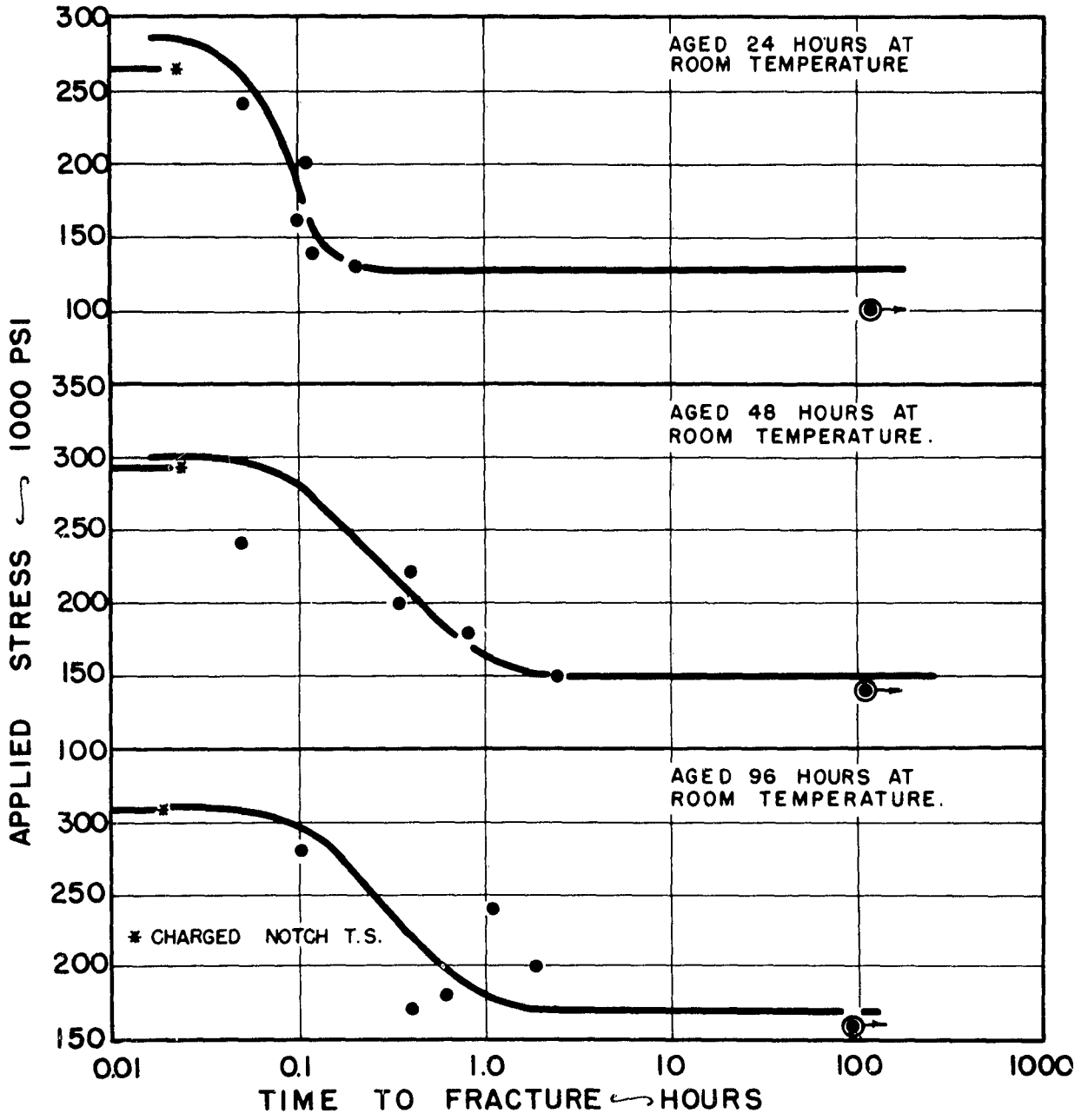


FIG.13: STRESS RUPTURE TESTS ON 4340 STEEL HEAT TREATED TO 270,000 PSI AND AGED AS INDICATED. (CHARGING CONDITION A, SHARP NOTCH SPECIMENS)

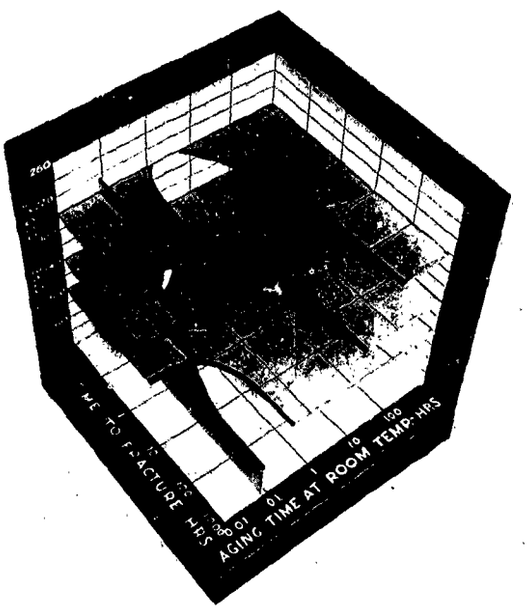


FIG. 14 : RELATIONSHIP BETWEEN APPLIED STRESS, AGING TIME AT ROOM TEMPERATURE AND TIME TO FAILURE. 230,000 PSI STRENGTH LEVEL. (CHARGING CONDITION A, SHARP NOTCH SPECIMENS)

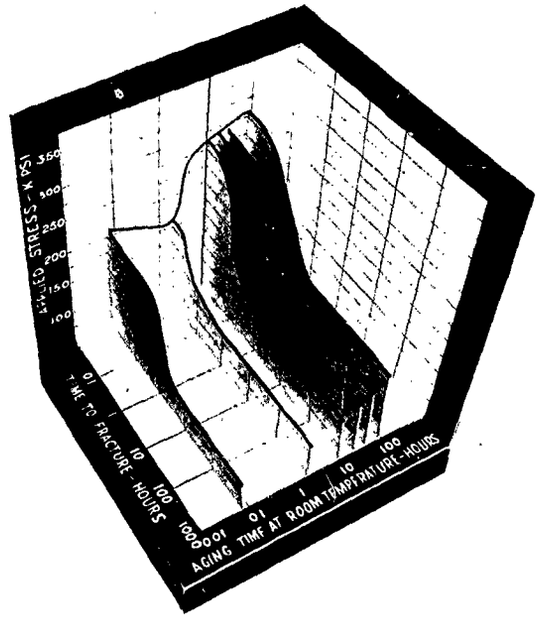


FIG. 15 : RELATIONSHIP BETWEEN APPLIED STRESS, AGING TIME AT ROOM TEMPERATURE AND TIME TO FAILURE. 270,000 PSI STRENGTH LEVEL, (CHARGING CONDITION A, SHARP NOTCH SPECIMENS)

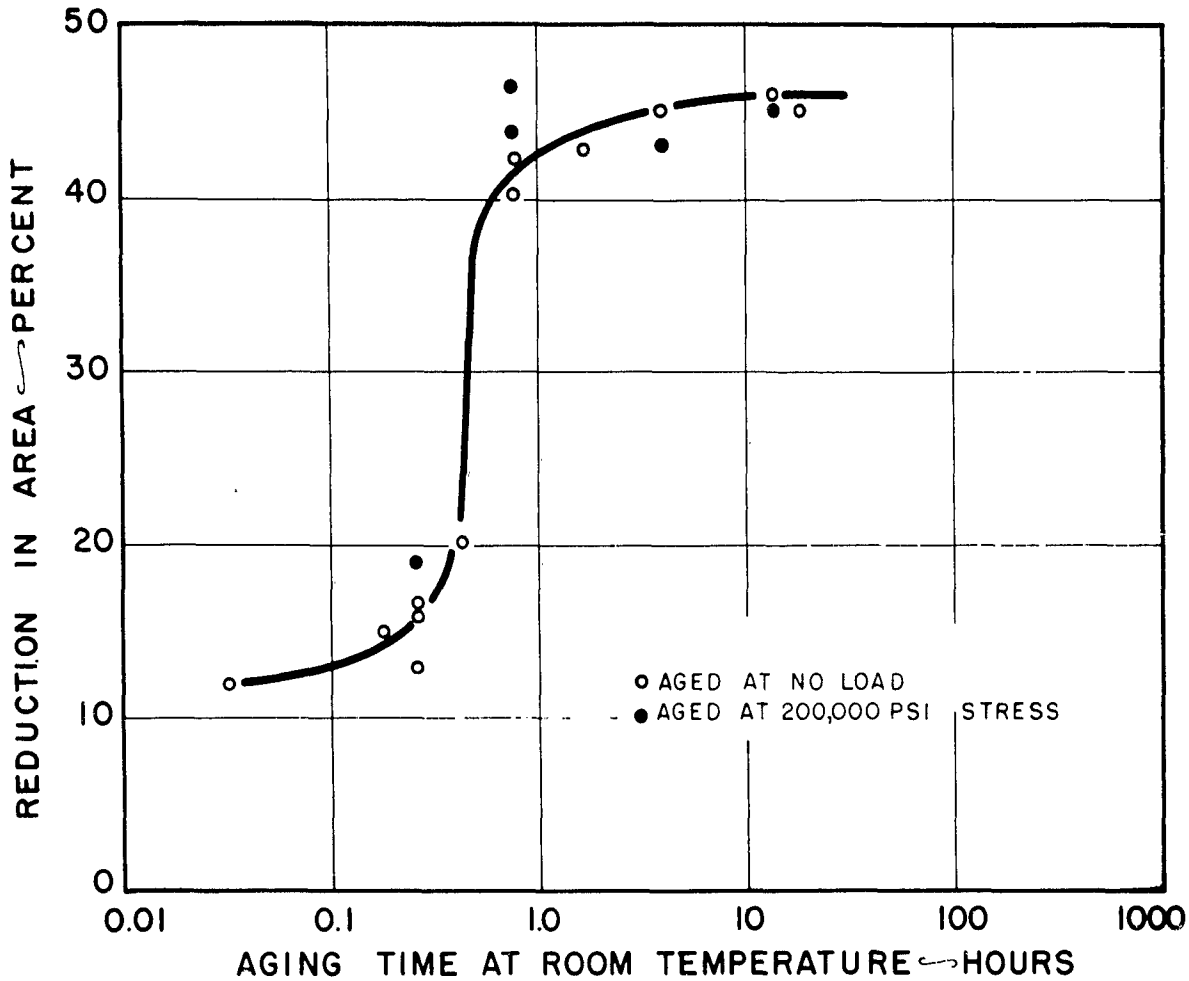


FIG.16: EFFECT OF AGING CHARGED SPECIMENS AT NO LOAD AND AT 200,000 PSI. APPLIED STRESS. UNNOTCHED SPECIMENS, 230,000 PSI. STRENGTH LEVEL. (CHARGING CONDITION A)

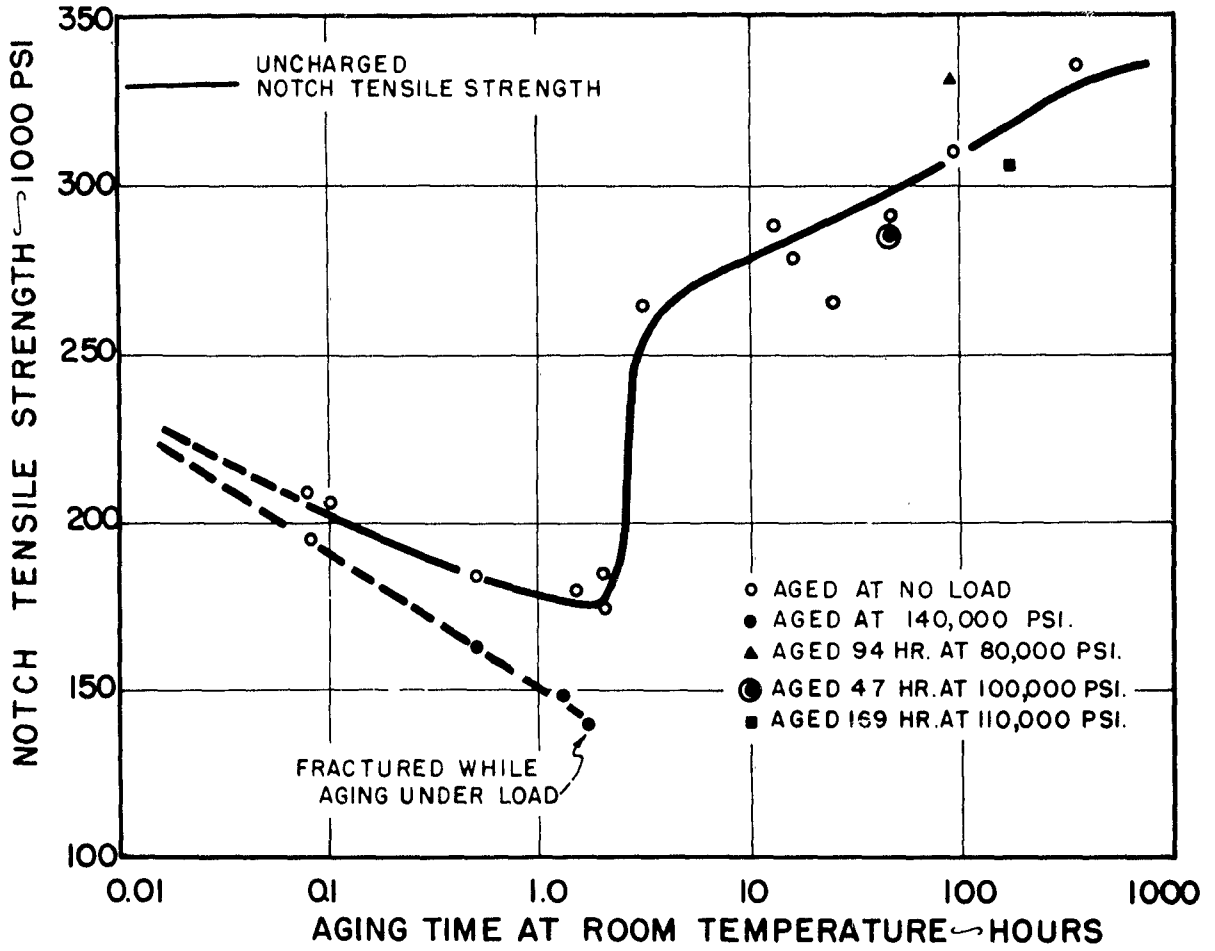


FIG.17: EFFECT OF AGING CHARGED SPECIMENS WITH AND WITHOUT APPLIED STRESS. SHARP NOTCH SPECIMENS HEAT TREATED TO 270,000 PSI. (CHARGING CONDITIONA)

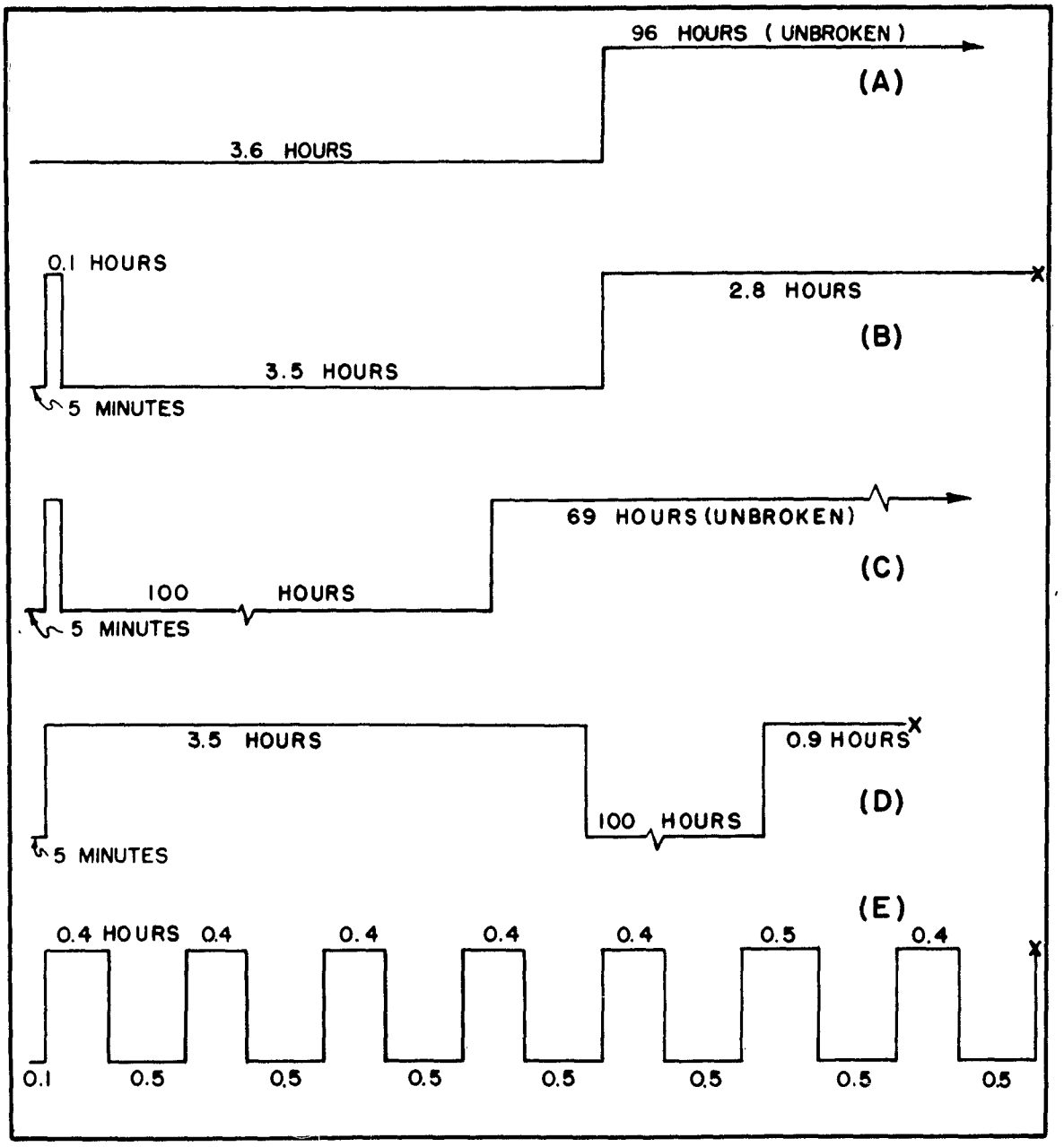


FIG.18: SCHEMATIC REPRESENTATION OF AGING TREATMENTS WITH AND WITHOUT APPLIED STRESS. CHARGING CONDITION **A**, SHARP NOTCH SPECIMENS, 230,000 PSI STRENGTH LEVEL. IN EACH CASE, THE LOWER LINE REPRESENTS AGING WITHOUT APPLIED STRESS AND THE UPPER LINE REPRESENTS AGING AT AN APPLIED STRESS OF 160,000 PSI.

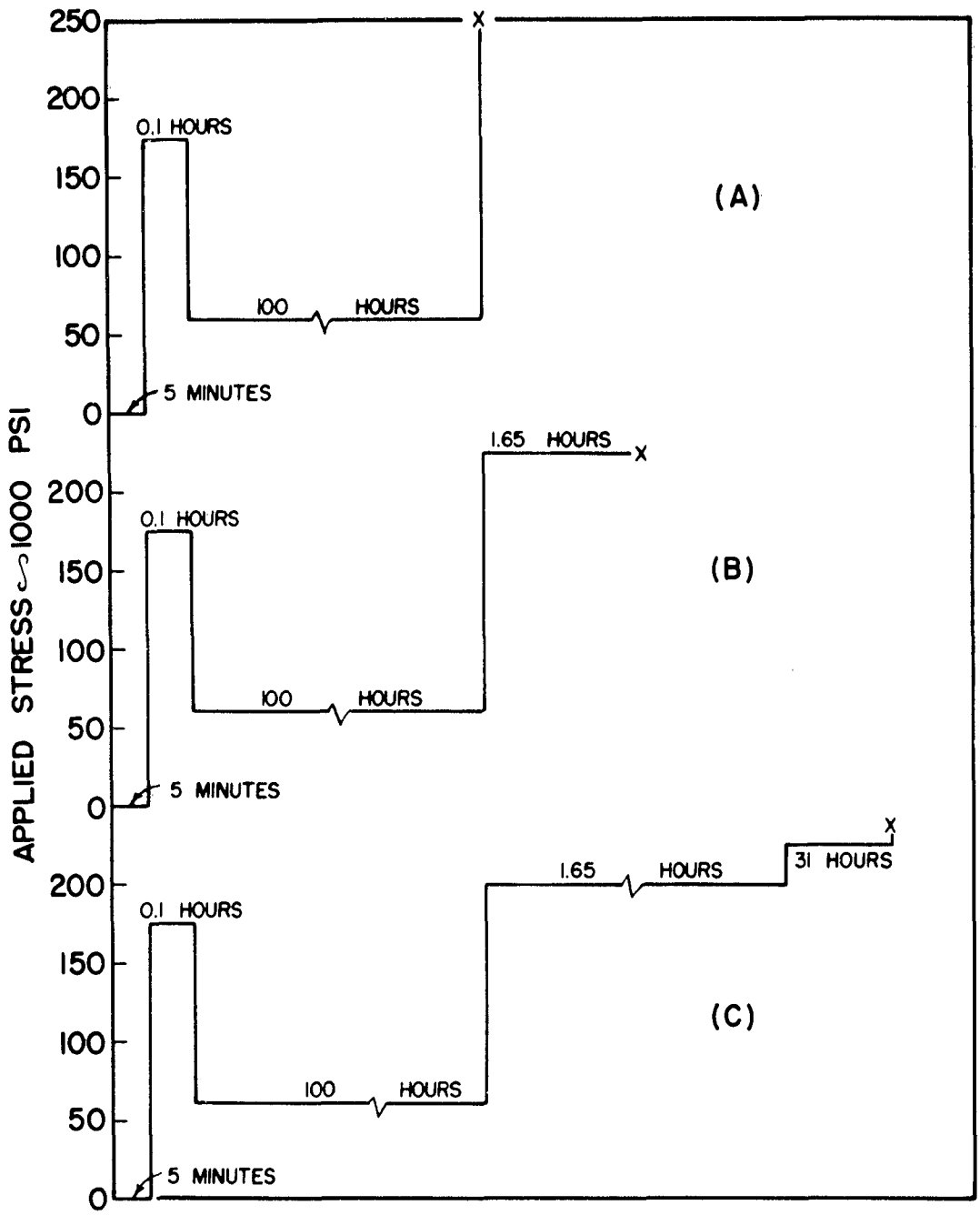


FIG.19: SCHEMATIC REPRESENTATION OF AGING TREATMENTS AT VARIOUS VALUES OF APPLIED STRESS. SHARP NOTCH SPECIMENS, 230,000 PSI. STRENGTH LEVEL, CHARGING CONDITION A.

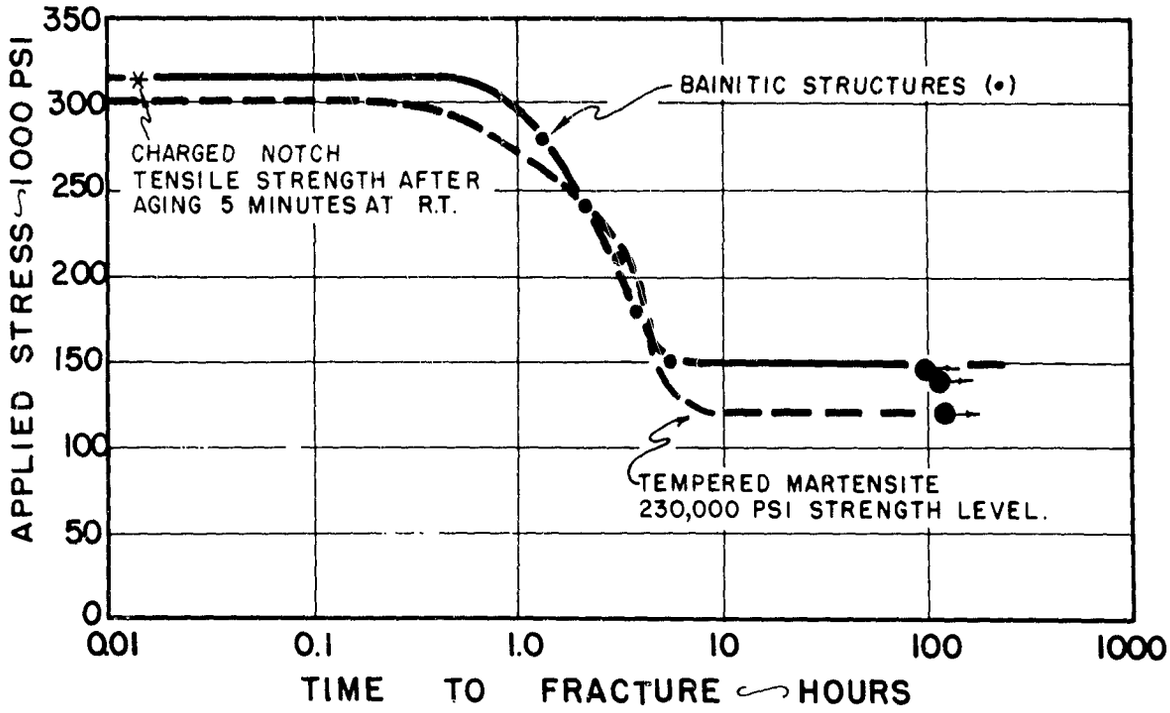


FIG.20: STRESS RUPTURE TESTS ON 4340 STEEL. TEMPERED BAINITIC STRUCTURE, 230,000 PSI. STRENGTH LEVEL. (CHARGING CONDITION A, SHARP NOTCH SPECIMENS AGED 5 MINUTES AT ROOM TEMPERATURE BEFORE TESTING)

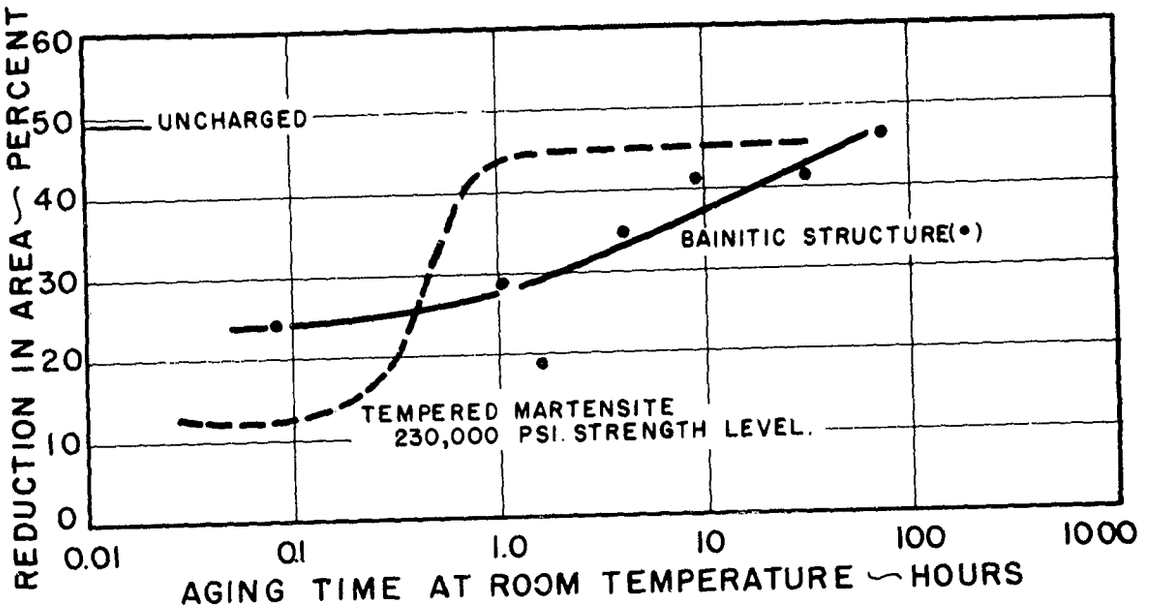


FIG.21: EFFECT OF AGING TIME ON DUCTILITY OF 4340 STEEL HEAT TREATED TO A 230,000 PSI. STRENGTH LEVEL. TEMPERED BAINITIC STRUCTURE. (CHARGING CONDITION A, UNNOTCHED TENSILE TESTS)

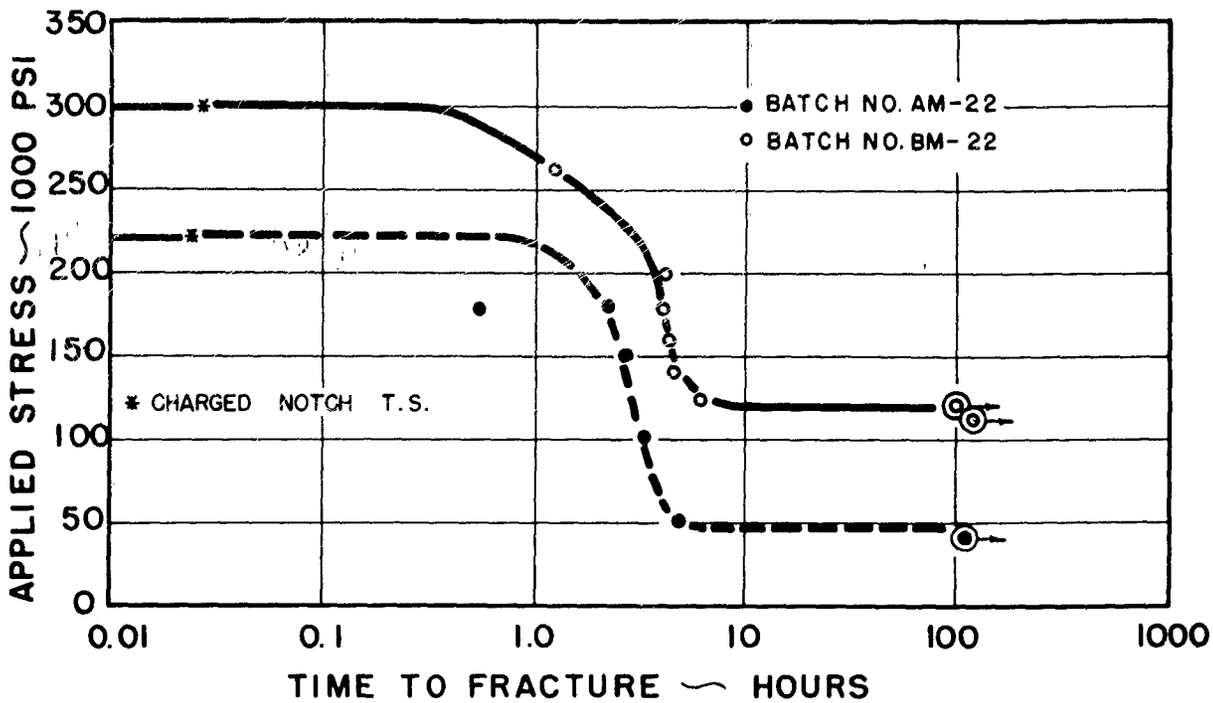


FIG.22: STRESS RUPTURE TESTS ON 4340 STEEL HEAT TREATED TO 230,000 PSI. (CHARGING CONDITION A, SHARP NOTCH SPECIMENS.) SEE TEXT FOR DETAILS.

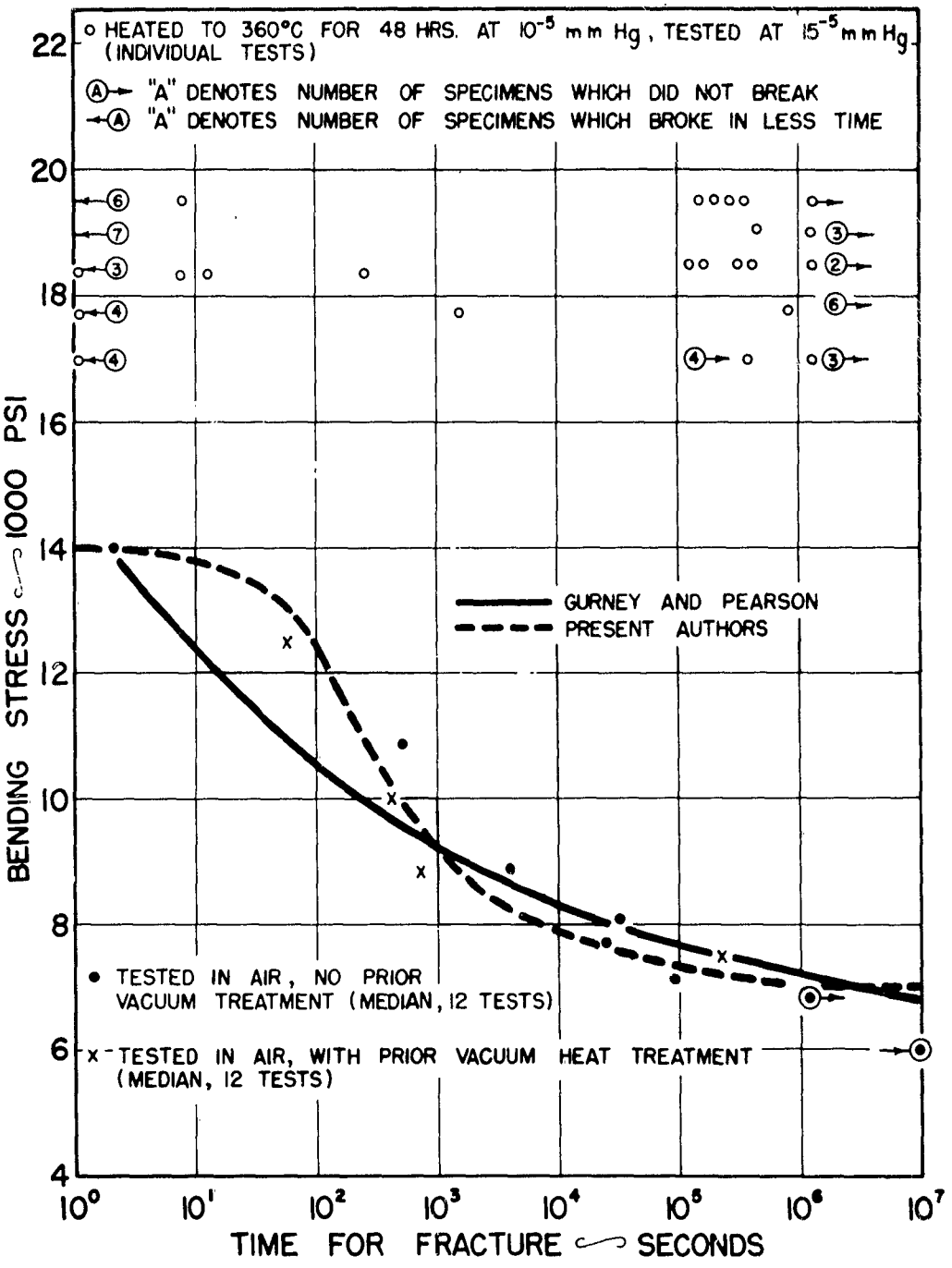


FIG. 23: RELATIONSHIP BETWEEN BENDING STRESS AND TIME FOR FRACTURE FOR ANNEALED GLASS RODS TESTED IN AIR AND IN VACUUM. [GURNEY AND PEARSON (41)]